Silver Nitrate–Alumina: A Chromatographic Reaction Medium for Conversion of 5-Halogenopent-2-enes into 1-Cyclopropylethyl Nitrate

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A chromatography column of 30% silver nitrate–neutral alumina provides a reactive surface for the ready conversion of 5-halogenopent-2-enes (1) into 1-cyclopropylethyl nitrate (2) upon elution with pentane. By this technique 5-bromopent-2-ene (1a) and 5-iodopent-2-ene (1b) are converted into (2) in 74 and 94% yield, respectively, in less than five minutes. 5-Chloropent-5-ene (1c) was unreactive under the same conditions. Reduced yields of (2) were observed when (1a) or (1b) were stirred, neat, with powdered silver nitrate. When acidic alumina was used to prepare the chromatography column and only partially dried, an efficient medium for hydrolysis to the corresponding alcohol resulted. Elution of (1a) with diethyl ether therefore gave 1-cyclopropylethanol (5) in 31% yield and elution of (2) with diethyl ether gave (5) in ca. 100% yield.

Liquid chromatography is a powerful tool for the separation of organic compounds but its utility as a reaction medium has received only cursory attention. One interesting example is the partial conversion of primary alkyl halides into the corresponding nitrate reported by Kuemmel using a silver nitrate–silica gel chromatography column.[1] Although limited in scope, this process constitutes a significantly milder method for the synthesis of nitrates, via a silver-mediated carbocation,[2] than those previously reported.[3] Liquid chromatography on silver nitrate–alumina is known to be an effective method for the separation of alkene–alkane mixtures, presumably by formation of a transient silver–alkene complex.[4] In addition, Posner has effected a number of interesting transformations utilizing activated acidic alumina.[5] It therefore appeared that alumina might provide a reactive surface for the chromatographic conversion of alkyl halides into nitrates. A particularly interesting class of alkyl halides are the 5-halogenopent-2-enes (1) which upon treatment with acid give cyclopropane derivatives via an intermediate cyclopropylmethyl cation (4).[6] Hanack, for example, has shown that (1) was converted into 1-cyclopropylethanol (5) by prolonged stirring in an aqueous suspension of silver oxide.[7] We therefore examined the reactivity of (1) on a 30% silver nitrate–neutral alumina chromatography column with the goal of converting (1) into 1-cyclopropylethyl nitrate (2). Our results are presented in the Table and clearly show that the conversion of (1) into (2) proceeds readily and in high yield.

(1)a; X = Br
 b; X = I
 c; X = Cl

(2) (3) (4) (5)

Results and Discussion

When 5-bromopent-2-ene (1a) was eluted with pentane through a chromatography column of 30% silver nitrate bound to neutral alumina[4] (residence time 5 min) a 74% yield of 1-cyclopropylethyl nitrate (2) was obtained along with 2% of pent-3-enyl nitrate (3). A 94% yield of (2) was realized when 5-iodopent-2-ene (1b) was eluted through the column. In sharp contrast to (1a) and (1b), 5-chloropent-2-ene (1c) was recovered unchanged upon elution, with no trace of (2) or (3). Use of the chromatography column appears to be the preferred technique since a slurry of silver nitrate and neutral alumina (not premixed) when stirred in pentane with (1a) gave only 17% yield of (2), 4% yield of (3), and 22% recovery of (1a). The poor mass-balance was presumably due to cationic polymerization at the surface of the silver nitrate, which was not a major problem with the chromatography technique. This is supported by the observation that (2) is completely stable to the alumina column. It appears that the alumina
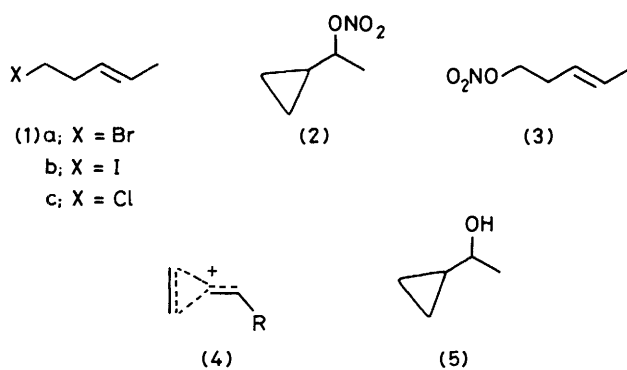
simply provides a greater surface area for reaction with silver nitrate.

Conditions for the conversion of simple alkyl halides into the corresponding nitrate usually involve prolonged heating of a solution of silver nitrate in acetonitrile or neat halide.[3] We therefore compared our chromatographic results with these traditional methods. Reaction of (1a) with powdered silver nitrate in acetonitrile (5 h) gave a mixture of (2) (25% yield) and (3) (60% yield). Prolonged exposure (120 h) likewise gave yields of 11% for (2) and 49% for (3). The iodide (1b), however, afforded (2) (69%) and only a 17% yield (3) after 5 h. The difference in product distribution is probably due to differences in the ion-pair transition state postulated for nitrate formation.[2] The chloride (1c) once again proved to be unreactive. When a suspension of powdered silver nitrate was stirred in neat (1a), a 74% yield of (2) was realized along with 4% of (3). The chloride (1c) again was unreactive and the iodide (1b) gave the expected nitrate (2), but in only 38% yield. In both the traditional approaches polymerization was a significant process and they are generally unsatisfactory as a synthetic approach to the nitrate (2). We noted that in acetonitrile (1a) gave (3) as the major product rather than (2) which was always the predominant product from the chromatography technique.

Since it appeared that the neutral alumina was an unreactive partner in the reaction medium, we prepared the column with acidic alumina and observed significant changes in product distribution. When the column material was only partially dried, henceforth referred to as ' wet ' silver nitrate–alumina, elution of (1a) with diethyl ether gave a 31% yield of the alcohol (5) as the only observed product, but polymerization was a major process. Scrupulous drying of the

**Table.** Reaction of 5-halogenopent-2-enes with silver nitrate

Halide	Method [b]	Contact time	Alumina	Yield (%)		
				(2)	(3)	(5)
(1a)	A	5 min	dry	74	2	—
	A	5 min	wet	69	—	—
	B	1 h	dry	74	—	—
	C	5 h	dry	25	60	—
	C	120 h	dry	11	49	—
	D	1 h	dry	17	4	—
	E	1 h	wet	9	—	8
	F	5 min	dry	—	32	18
	F	5 min	wet	—	—	31
(1b)	A	5 min	dry	94	—	—
	B	5 h	dry	47	—	—
	C	5 h	dry	69	17	—
(1c) [a]	A	5 min	dry	—	—	—
	B	1 h	dry	—	—	—
	C	5 h	dry	—	—	—

[a] Only starting material was recovered, unchanged. [b] Method A: Chromatography on 30% silver nitrate–neutral alumina, pentane eluant. Method B: Silver nitrate suspended in the halide, neat, ambient temperature. Method C: Silver nitrate dissolved in acetonitrile, ambient temperature. Method D: Silver nitrate and neutral alumina suspended in pentane, ambient temperature. Method E: Silver nitrate and acidic alumina suspended in pentane, ambient temperature. Method F: Chromatography on 30% silver nitrate–acidic alumina, ether eluant.

silver nitrate–acidic alumina adsorbent and elution of (1a) with diethyl ether gave yields of 32% for (3) and 18% for (5). This is analogous to results obtained when (1) is treated with mineral acid.[3] To probe further the function of the acidic alumina we eluted pure (2) through the 'wet' column with diethyl ether and obtained (5) in ca. quantitative yield. The acidic alumina, in the presence of water, is the key to this transformation since elution of (2) through a 'wet' or 'dry' silver nitrate–neutral alumina column gave only unchanged (2). Previous reports of hydrolysis of alkyl nitrates to the corresponding alcohol required solutions of aqueous acid.[8] The 'wet' silver nitrate–acidic alumina column therefore provides a reaction medium for particularly mild hydrolysis of (2). The power of the chromatography technique was once again demonstrated when a slurry of silver nitrate and acidic alumina (not premixed) was stirred in diethyl ether with (1a) and only an 8% yield of (5) and 9% of (3) were obtained with only 10% of (1a) recovered.

Identification of (2) and (3) as the nitrate esters was straightforward. The i.r. spectra exhibited the three strong absorption bands at 864, 1 290, and 1 640 cm⁻¹ characteristic of alkyl nitrates.[9] The ¹H n.m.r. spectrum of (2) exhibited signals due to cyclopropyl protons at δ 0.1—1.1 and the methyl protons at δ 1.35. The proton on the nitrate-bearing carbon resonated at δ 4.09—4.60, consistent with n.m.r. data for other alkyl nitrates.[10] Fragmentation patterns reported for alkyl nitrates [11] were observed with (2) and (3) in their mass spectra. The parent ion is very weak but the cyclopropyl fragment, [C₃H₅]⁺, is prominent and important nitrate-bearing fragments arise from loss of cyclopropyl and methyl moieties, giving [CH₃CHONO₂]⁺ and [C₃H₅CHONO₂]⁺, respectively.

It is clear that the reactivity of homoallylic halides such as (1) to silver nitrate is: iodide > bromide ≫ chloride, with the chloride being unreactive. These results are explained by Kornblum's 'push–pull' mechanism in which the ion pair (6) is the key transition state for formation of nitrates from

$$[O_2NO^- \ R^+ \ X—Ag]$$

(6)
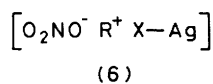
halides.[2] The chromatography technique is clearly superior to reaction of (1) with silver nitrate, either neat or in acetonitrile, since the yields of (2) are generally higher, yields of (3) lower, and there is less polymerization of (1). Reaction on the column occurs in less than five minutes, essentially as fast as the halide can be pushed through the adsorbent using medium-pressure chromatography techniques.

The 'wet' acidic alumina column offers a fast and mild method for the hydrolysis of nitrate (2) to the alcohol (5). It appears that (2) is formed 'in situ,' and is then subjected to hydrolysis, catalysed by the acidic alumina. Elution of (1a) through a 'wet' silver nitrate–neutral alumina column gave only (2) with no trace of (5).

In contrast to the previous, rather harsh methods for the conversion of alkyl halides into nitrates, the chromatographic techniques described herein allow a ready preparation of either (2) or (3) in good yield. In addition, the nitrate (2) is hydrolysed to (5) under remarkably mild conditions.

Experimental

The silver nitrate, zinc bromide, and zinc chloride used in this study were obtained from Fisher Scientific. The aluminium oxide used for preparation of the columns was Allied Chemical neutral alumina (ignited powder) and Fluka 506C, activity I, acidic alumina. 1-Cyclopropylethanol (5) was obtained from Aldrich Chemicals. All ¹H n.m.r. spectra were recorded on a Varian EM-360 n.m.r. spectrometer at 60 MHz using solutions in CDCl₃ with tetramethylsilane as internal standard. Mass spectra were recorded in an A.E.I. MS-9 mass spectrometer and i.r. spectra were recorded for neat films on a Perkin-Elmer IR-283 spectrophotometer. Ether refers to diethyl ether.

5-Bromopent-2-ene (1a).—Addition of zinc bromide (184.8 g, 0.82 mol), in portions, to 48% HBr (370 ml, 1.21 mol) at −10 °C was followed by addition (during 5 min) of 1-cyclopropylethanol (2.0 g, 23 mmol). The resultant slurry was vigorously stirred, warmed to 0 °C, and stirred for an additional 1 h. Extraction with pentane (30 ml) was followed by addition of ice-cold water (250 ml) overlaid with pentane

(500 ml). The pentane layer was washed in turn with (150 ml) brine, saturated sodium hydrogen carbonate (2 × 150 ml), and brine (2 × 150 ml), dried (MgSO₄), and the solvents were removed under reduced pressure. Distillation of the residue through a 15 cm Vigreux column gave 5-bromopent-2-ene (1a) (2.3 g, 67%), n_D^{18} 1.4710; b.p. 121—121.5 °C [lit.,[12] 125—126 °C]; δ 1.6 (3 H, distorted d), 2.3—2.7 (2 H, m), 3.1—3.4 (2 H, t, J 3.0 Hz), and 4.9—5.6 (2 H, m); $v_{max.}$ 3 020, 1 670, 1 450, 1 265, 1 210, 970, and 640 cm⁻¹; m/z 150 ($M^+ + 2$, 11%), 148 (M^+, 12), 69 ($M^+ - 79$, 100), 55 (65), 53 (14), 42 (11), 41 (79), 39 (37), and 29 (21).

5-Iodopent-2-ene (1b).—To a solution of triphenylphosphine (14.0 g, 53 mmol) and 1-cyclopropylethanol (5) (4.3 g, 50 mmol) in dry dimethylformamide (DMF) (125 ml) cooled to —40 °C (diglyme–CO₂) was added iodine dissolved in a minimal amount of DMF until the reaction mixture maintained a faint colour of excess of iodine. The mixture was warmed to ambient temperature and flash distilled into a chilled receiver (−78 °C), and the material boiling below 33 °C (0.15 mmHg) was poured into ice-cold water (300 ml). The organic material which separated was dissolved in (50 ml) ether, dried (CaCl₂), and the solvents were evaporated under reduced pressure. Distillation gave 5-iodopent-2-ene (1b) (5.3 g, 54%), b.p. 27—27.2 °C at 2.7 mmHg [lit.,[14] 53—55 °C at 15 mmHg]; n_D^{18} 1.5235 [lit.,[14] n_D^{20} 1.5227]; δ 1.6 (3 H, distorted d), 2.2—2.7 (2 H, m), 3.0 (2 H, distorted t), and 4.9—5.65 (2 H, m); m/z 196 (M^+, 2%), 70 ($M^+ - 126$, 12), 69 ($M^+ - 127$, 100), 67 (10), 55 (12), 53 (13), 42 (8), 41 (88), 39 (34), and 29 (13) (Found: M^+, 195.9753. Calc. for C_5H_9I: M, 195.9755).

5-Chloropent-2-ene (1c).—To Lucas' reagent (50 g) [prepared from zinc chloride (34 g, 0.25 mol), and conc. HCl (26.3 g, 0.25 mol)], cooled in an ice-bath, was added dropwise 1-cyclopropylethanol (5) (6 g, 70 mmol). After being stirred at ambient temperature for 1 h, the mixture was poured into ice-cold water (250 ml) overlaid with ether (50 ml). The ether phase was separated, dried (MgSO₄), and the solvent was removed under reduced pressure. Double distillation through a 15 cm Vigreux column gave 5-chloropent-2-ene (1c) in 10% yield, b.p. 107 °C [lit.,[8] 106—107 °C; lit.,[13] 107—108 °C]; δ 1.6 (3 H, distorted d), 2.2—2.7 (2 H, m), 3.2—3.55 (2 H, t, J 3.0 Hz), and 4.9—5.64 (2 H, m).

Preparation of 30% Silver Nitrate–Alumina Chromatography Adsorbent.[4]—The adsorbent was prepared, with exclusion of light, by rotating a slurry consisting of neutral aluminium oxide (200 g) and a solution of silver nitrate (100 g) in water (180 ml) for 1 h. The slurry was rotated in a water-bath at 50—60 °C, under aspirator vacuum, until all water had been removed. The adsorbent was then dried in a vacuum oven (65 °C; 1 mmHg) for 12 h and stored in the dark.

1-Cyclopropylethyl Nitrate (2).—(a) *Method A. From column chromatography with silver nitrate–neutral alumina.* (i) *From* (1a). Pressurized elution (with argon) of (1a) (0.62 g, 4.2 mmol) through a 30 × 2 cm column of silver nitrate–neutral alumina with pentane as eluant gave an eluate collected in 50 ml fractions. Removal of pentane under reduced pressure from the first fraction gave an oil consisting of 2.6% (3) and 97.4% (2) (by n.m.r. spectroscopy). Distillation (15 cm Vigreux column) gave 1-cyclopropylethyl nitrate (2) (0.4 g, 74%), b.p. 42—43 °C at 12 mmHg; n_D^{20} 1.4325; δ 0.1—1.1 (5 H, m, C_3H_5), 1.35 (3 H, d, J 3.1 Hz, CH₃), and 4.09—4.60 (1 H, d of q, J 3.1 and 4.0 Hz, CHONO₂); $v_{max.}$ 3 100, 1 640, 1 455, 1 290, and 864 cm⁻¹; m/z 131 (M^+, 0.01%), 116 ($M^+ - 15$, 5), 90 ($M^+ - 41$, 7), 55 ($M^+ - 76$, 100), 76 (10), 68 (13),

67 (13), 56 (13), 54 (10), 53 (20), 46 (53), 43 (57), 42 (18), 41 (80), 39 (47), 30 (27), and 29 (73) (Found: m/z 116.1351. $C_4H_6NO_3$ requires m/z, 116.0348) (Found: m/z 90.0194. $C_2H_4NO_3$ requires m/z 90.0191).

(ii) *From* (1b). Elution of (1b) (1.3 g, 6.7 mmol) with pentane, under the same conditions, gave (2) (0.83 g, 94%).

(iii) *From* (1c). Elution of (1c) (0.25 g, 2.4 mmol) with pentane, under the same conditions, gave only unchanged (1c), with no trace of (2) or (3).

(b) *Method B. From powdered silver nitrate in the halide, neat.* (i) *From* (1a). A slurry of dry, powdered silver nitrate (1.15 g, 6.78 mmol) and (1a) (1.0 g, 6.79 mmol) was stirred at ambient temperature for 1 h (CaSO₄ drying tube), with exclusion of light. The liquid portion was decanted and the remaining yellow solids were washed with several portions of pentane which was then decanted. Evaporation of the combined pentane fractions under reduced pressure afforded (2) (0.66 g, 74%).

(ii) *From* (1b). Similar reaction of (1b) (1.17 g, 6.0 mmol) with silver nitrate (1.02 g, 6.0 mmol) gave (2) (0.37 g, 47%) and (1b) (0.42 g, 35% recovery), after distillation.

(iii) *From* (1c). Similar reaction of (1c) (0.40 g, 3.71 mmol) with silver nitrate (0.63 g, 3.72 mmol) gave only unchanged (1c).

(c) *Reaction of* (1a) *with silver nitrate–' wet ' neutral alumina column.* A column of silver nitrate–neutral alumina was prepared as described above except that the adsorbent was dried for only 2 h at 110 °C (1 atm) prior to use. When (1a) (0.54 g, 3.6 mmol) was eluted through a 30 × 2 cm column of silver nitrate–' wet ' alumina neutral with pentane (100 ml) followed by ether (100 ml), only the pentane fraction afforded a product. Evaporation of solvents at reduced pressure gave a 92 : 8 mixture (by n.m.r. spectroscopy) of (2) : (1a) (0.33 g). This corresponds to a yield of (2) of 2.5 mmol (69%).

(d) *Method C. From silver nitrate dissolved in acetonitrile.* (i) *From* (1a). To a solution of silver nitrate (1.16 g, 6.8 mmol) in dry, distilled acetonitrile (2.5 ml) was added (1a) (1.0 g, 6.7 mmol). After 5 h at ambient temperature the silver bromide was filtered off and washed with several 50 ml portions of ether. The filtrate was poured into ice-water (200 ml) and the oil which separated was extracted with CH₂Cl₂ (2 × 25 ml). Drying (MgSO₄) and removal of solvents under reduced pressure gave a 29 : 71 (n.m.r.) mixture of (2) and (3) (0.75 g). Distillation afforded (2) (0.22 g, 25%) and *pent-3-enyl nitrate* (3) (0.53 g, 60%), b.p. 70—73 °C at 50 mmHg; δ 1.6 (3 H, distorted d, CH₃), 2.15—2.61 (2 H, m, CH₂CH=CH), 4.1—4.5 (2 H, t, J 3.0 Hz, CH₂ONO₂), and 4.9—5.6 (2 H, m, CH=CH); $v_{max.}$ 3 100—2 850, 1 625, 1 430, 1 275, 960, 860, and 750 cm⁻¹; m/z 131 (M^+, 0.1%), 55 ($M^+ - 76$, 100), 106 (4), 91 (7), 76 (9), 69 (10), 68 (5), 56 (8), 54 (7), 53 (12), 51 (4), 46 (32), 43 (21), 41 (25), 39 (25), 30 (11), and 29 (40) (Found: M^+, 131.0575. $C_5H_9NO_3$ requires M, 131.1583) (Found: m/z 76.0038. CH₂NO₃ requires m/z 76.0035).

(ii) *From* (1b). Reaction of (1b) (2.5 g, 12.7 mmol) with silver nitrate (2.20 g, 12.7 mmol) in acetonitrile (5 ml) for 5 h with work-up as above gave an 8 : 2 mixture of (3) : (2) (1.4 g). This corresponds to 69% yield for (2) and 17% yield for (3).

(iii) *From* (1c). Reaction of (1c) (2.5 g, 3.1 mmol) with silver nitrate (0.54 g, 3.2 mmol) in acetonitrile (1.5 ml) for 5 h with work-up as above gave only unchanged (1c).

(iv) *From* (1a) [*longer reaction time than in* (i)]. Reaction of silver nitrate (0.65 g, 3.85 mmol) with (1a) (0.52 g, 3.5 mmol) in acetonitrile (1 ml) for 120 h with work-up as above afforded an 82 : 18 mixture of (3) : (2) (0.27 g). This corresponds to 49% yield for (3) and 11% yield for (2).

(e) *Method D. From silver nitrate and neutral alumina*

suspended in pentane. To a solution of (1a) (0.35 g, 2.32 mmol) in pentane (2 ml) was added neutral aluminium oxide (0.30 g, 2.9 mmol) and dry, powdered silver nitrate (0.40 g, 2.35 mmol). The slurry was stirred at ambient temperature for 1 h, with exclusion of light, the liquid was decanted, and the yellow solid was washed with pentane (5 × 5 ml). Evaporation of the washings gave a mixture (0.141 g) of (2) : (3) : (1a) in the proportions 39.5 : 9.3 : 51.2 (n.m.r.). This corresponds to yields of 17% for (2) and 4% for (3), and 22% recovery of (1a).

(f) *Method E. From silver nitrate and acidic alumina suspended in pentane.* To a solution of (1a) (0.42 g, 2.82 mmol) in pentane (2 ml) was added acidic aluminium oxide (0.15 g, 1.47 mmol) and dry, powdered silver nitrate (0.48 g, 2.82 mmol). Work-up as in Method D afforded a 33 : 30 : 37 mixture (0.09 g) of (2), 1-cyclopropylethanol (5), and (1a) respectively. This corresponds to yields of 9% for (2) and 8% for (5), and 10% recovery of (1a).

1-Cyclopropylethanol (5).—(a) *Method F. From column chromatography with silver nitrate–acidic alumina and* (1a). A column of silver nitrate–alumina was prepared as above except that acidic alumina was used rather than neutral alumina and the adsorbent was dried for 2 h at 110 °C (1 atm) prior to use. Henceforth this is referred to as ' wet ' acidic alumina.

When (1a) (1.0 g, 6.7 mmol) was eluted (pressurized with argon) through a 30 × 2 cm column of silver nitrate–' wet ' acidic alumina with pentane (600 ml) followed by ether (200 ml), only the ether fractions contained products. Evaporation of the ether fractions at reduced pressure afforded 1-cyclopropylethanol (5) (0.18 g, 31%) after distillation, b.p. 121—122 °C [lit.,[8] 121—122 °C; lit.,[15] 122—123 °C]; n_D^{19} 1.4319; δ 0.1—1.1 (5 H, m, C₃H₅), 1.25 (3 H, d, *J* 3.1 Hz, CH₃), 2.6 (1 H, s, OH), and 3.0 (1 H, m, C*H*OH); ν_max. 3 370, 3 100, 3 020, 2 990, 2 940, 2 780, 1 370, 1 300, 1 100, 1 080, 1 050, 1 020, 990, and 945 cm⁻¹.

(b) *From reaction of* (2) *with* ' *wet* ' *acidic alumina.* When (2) (0.085 g, 0.65 mmol) was eluted (pressurized with argon) through a 30 × 2 cm column of silver nitrate–' wet ' acidic alumina with pentane (100 ml) followed by ether (100 ml), only the ether fractions afforded products. Evaporation of the ether fractions under reduced pressure gave (5) (0.06 g, 98.5%).

(c) *From reaction of* (1a) *with* ' *dry* ' *acidic alumina.* The acidic alumina adsorbent was prepared as described above but was dried in a vacuum oven (110 °C; 1 mmHg) for 20 h prior to use.

When (1a) (1.1 g, 7.4 mmol) was eluted (pressurized with argon) through a 30 × 2 cm column of silver nitrate–' dry ' acidic alumina with pentane (150 ml) followed by ether (150 ml), the pentane fractions contained an unidentifiable material (0.17 g). The ether fractions, after evaporation under reduced pressure, afforded an 8 : 2 mixture of (3) : (5) (0.43 g). This corresponds to yields of 0.37 g (32%) for (3) and 0.11 g (18%) for (5).

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