ELSEVIER

Journal of Fluorine Chemistry 115 (2002) 101–105

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

Short communication

New aromatic pentafluoro-λ^6-sulfanyl (SF_5) derivatives, m-$SF_5(CF_2)_2C_6H_4X$: ($X = N_3$, Br, $OC(O)CH{=}CH_2$, $CH{=}CH_2$)

R.W. Winter, S.W. Winner, D.A. Preston, J. Mohtasham, J.A. Smith, G.L. Gard*

Department of Chemistry, Portland State University, 1719 SW 10th Avenue, P.O. Box 751, Portland, OR 97207, USA

Received 8 January 2002; received in revised form 21 March 2002; accepted 25 March 2002

Abstract

Preparation of the following new m-$SF_5CF_2CF_2C_6H_4X$ derivatives has been achieved: $X = N_3$(**2**), Br(**3**), $OC(O)CH{=}CH_2$(**4**), $CH{=}CH_2$(**5**). The compounds were characterized by their respective IR, NMR, mass spectra (MS) and high resolution mass spectrometry (HRMS). An improved yield of $SF_5(CF_2)_2C_6H_5$ (**1**) is also reported along with the synthesis of the polyacrylate (**6**) and polystyrene (**7**) from their respective monomers. © 2002 Published by Elsevier Science B.V.

Keywords: Pentafluorothiofluoroalkyl benzene derivatives; SF_5; Acrylate/stryrene monomers and polymers

1. Introduction

The incorporation of the SF_5-group into organic systems imparts a number of useful properties that include low wettability, low dielectric constant, high thermal stability, high chemical resistance, low refractive index and low surface energy [1–4]; these properties are also found in polymeric films containing terminal SF_5-groups [5–8]. It should be noted that the interest in SF_5-aromatic chemistry has extended to the fine chemicals industry [9].

Recently, we reported the synthesis of a new class of ω-SF_5-perfluoroalkylbenzene compounds, $SF_5(CF_2)_nC_6H_5$ with $n = 2,4,6,8$ [10] and also on a number of new m-$SF_5(CF_2)_2C_6H_4X$ derivatives of synthetic value [11].

We have improved on the synthesis of $SF_5(CF_2)_2C_6H_5$ (**1**) and have extended its chemistry by preparing several important derivatives, especially ones with polymerizable functional groups.

2. Results and discussion

We have found that the yield of $SF_5(CF_2)_2C_6H_5$ (**1**) can be increased to 74% by using a Parr Bomb reactor (300 ml) that is stirred under an argon atmosphere for 14 days at 145 °C; previous work using a 350 ml Pyrex-glass Carius Tube gave yields of only 30% [10].

Several new and important derivatives of (**1**) have been synthesized (Scheme 1). The first three steps have already been reported [11]; the azide derivative (**2**) was formed from the corresponding diazonium intermediate (4i); the acrylate (**4**) from the phenol via steps 5i–7i and the styrene derivative from the bromide (**3**), steps 9i–10i [12,13]. The polymeric acrylate (**6**) and styrene (**7**) were prepared (steps 8i and 11i). The polymers were soluble in the heated benzene solution; the isolated (**6**) was a solid and (**7**) a viscous oil. The viscous oil solidified upon exposure to air for several weeks. By comparison, the polymerization of m-$CF_3C_6H_4CH{=}CH_2$ gave a polymer with a softening range of 130–155 °C [14]; our polymer (**7**) has a softening range of 70–90 °C and is stable to at least 300 °C.

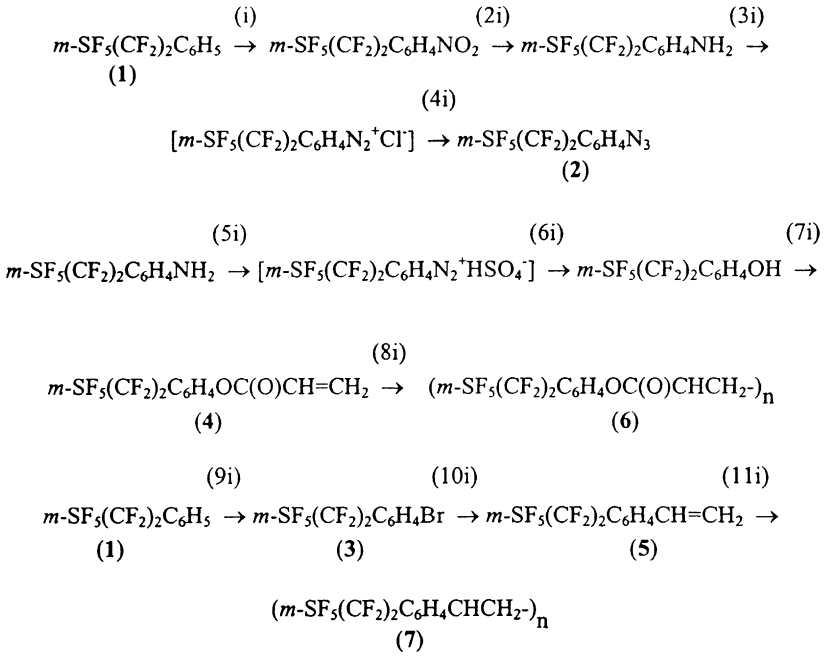
The infrared (IR), mass spectral (MS) and HRMS data for the new compounds (**2**–**5**) are listed in Table 1. Their IR spectra showed the characteristic intense SF_5 bands in the 800–900 cm^{-1} and 605–613 cm^{-1} regions [15]. The strong absorption peaks in the 1100–1300 cm^{-1} region were attributed to the C–F stretching vibrations [16]. The absorption band for compound (**2**) at 2120 cm^{-1} is assigned to the azido stretching mode [17]. For the acrylate monomer (**4**), the vinyl stretching mode is located at 1632 cm^{-1}; this band is absent in the polymeric solid (**6**). The carbonyl absorption (**6**) is found at 1752 cm^{-1} and for the polymer (**7**) at 1761 cm^{-1}. For the styrene monomer (**5**) the vinyl stretching mode is at 1636 cm^{-1}; it is absent in the polymer (**7**).

The ^{19}F NMR results for compounds **2**–**5** are included in Table 2. The values for the chemical shifts and coupling

---

[*] Corresponding author. Tel.: +1-503-725-4274; fax: +1-503-725-3888.
E-mail address: gardg@pdx.edu (G.L. Gard).

0022-1139/02/$ – see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-1139(02)00059-3



Scheme 1. Synthesis of compounds **2**–**7**: (i) HNO_3, 0–5 °C, 2 h; (2i) $HCl/SnCl_2$, 75–80 °C, 48 h, NaOH; (3i) $HCl/NaNO_2$, 0 °C, 0.5 h; (4i) NaN_3, 0–5 °C. 0.5 h, warmed to room temperature, 1 h; (5i) $H_2SO_4/NaNO_2$, 0 °C, 0.67 h; (6i) H_2SO_4/H_2O, 120–145 °C, 1 h; (7i) $H_2C{=}CHC(O)Cl/(CH_3CH_2)_3N/CH_2Cl_2$, −78 °C to room temperature, 3 h; (8i) $(CH_3)_3COOC(CH_3)_3/C_6H_6$, 93–102 °C, 4 days; (9i) mod. Wohl-Ziegler bromination, room temperature, 8 h; (10i) $(n\text{-}C_4H_9)_3SnCH{=}CH_2$, $Pd[P(C_6H_5)_3]_4$, $CH_3C_6H_5$, reflux, 24 h; (11i) $(CH_3)_3COOC(CH_3)_3/C_6H_6$, 104–120 °C, 5 days.

constants agree with reported values for other $SF_5CF_2CF_2$ derivatives [10,11]. The ^1H NMR data are summarized in Table 2; aromatic protons have chemical shifts ranging between 7.22 and 7.76 ppm and appear as a singlet (H2), triplet (H5) and two doublets (H4,H6). The coupling constants between the ring protons range between 7.7 and 8.2 Hz; compounds (**4**) and (**5**) show in addition the vinyl grouping with typical splitting, positioning and coupling.

The major mass spectral peaks for each compound (**2**–**5**) are listed in Table 1. In addition to the parent ion, additional peaks are found that support the assigned structure. In lieu of elemental analyses, the molecular weight of the compounds (**2**–**5**) were determined to seven significant places by high resolution mass spectrometry (HRMS). The IR, NMR, and HRMS analyses were carried out on samples that were shown to be pure via GC-MS.

3. Experimental details

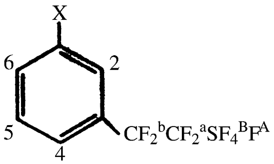
The reactants *N*-bromosuccinimide, $[(C_6H_5)_3P]_4Pd$, $(n\text{-}C_4H_9)_3SnCH{=}CH_2$, and acryloyl chloride were purchased from Aldrich. The compounds $m\text{-}SF_5(CF_2)_2C_6H_4X$ ($X = NH_2$, OH) were prepared according to the literature methods [11].

IR spectra were obtained using a Perkin-Elmer 2000 FTIR system operating at 2.0 cm^{-1} resolution. For liquid and solid samples, KBr plates were used. NMR spectra were obtained using a Varian EM-390 spectrometer operating at 84.6 MHz

Table 1
IR, MS and HRMS data (compounds **2**–**5**)

Compound	IR (cm^{-1})	MS (*m*/*z*, %)	HRMS		
			Formula	Calculated	Found
2	2120 (N_3), 1291, 1255, 1201, 1161, 1132, 1116 (C–F), 877, 845, 809, 605 (S–F)	345 (M^+, 6); 317 ($(M\text{–}N_2)^+$, 51); 190 ($(M\text{–}N_2\text{–}SF_5)^+$, 20); 140 ($(CF_2C_6H_2N)^+$, 100); 127 ($SF_5^+$, 6)	$C_8H_4F_9SN_3$	344.99822	344.99788
3	1283, 1262, 1200, 1163, 1120 (C–F), 878, 817,607 (S–F)	384/382 (M^+, 27/25); 207/205, ($(M\text{–}SF_5CF_2)^+$, 99/100); 127 (SF_5^+, 6)	$C_8H_4F_9SBr$	381.90734	381.90735
4	1752 (CO), 1632 ($CH{=}CH_2$), 1294, 1277, 1240, 1196, 1146, 1117 (C–F), 876, 609 (S–F)	372 (M^+, 5); 227 ($(M\text{–}HSF_6)^+$, 8); 89 (SF_3^+, 3); 55 ($(CH_2CHCO)^+$, 100)	$C_{11}H_7O_2F_9S$	374.00231	374.00288
5	1636 ($CH{=}CH_2$), 1296,1272, 1198, 1157, 1116 (C–F), 877, 845, 809, 605 (S–F)	330 (M^+, 5); 203 ($(M\text{–}SF_5)^+$, 8; 153 ($(M\text{–}SF_5CF_2)^+$, 100, 127 (SF_5^+, 4)	$C_{10}H_7F_9S$	330.01248	330.01265

Table 2
Proton and fluorine NMR data



	δ_2	δ_4	δ_5	δ_6	φ_A	φ_B	φ_a	φ_b
X = Br (**3**)	7.76, s, 1.0H	7.55, d, $J_{45} = 7.7$ Hz, 1.0H	7.38, t, $J \approx 8.1$, 1.0H	7.72, d, $J_{56} = 8.05$, 1.0H	66.8, t of 9 lines, $J_{AB} = 149$, $J_{Aa} = 4.9$, 1.0F	45.7, skewed d-m, 4.0F	−96.4, p-d, $J_{Aa} = 4.9$, $J_{aB} = 13.6$, 2.1F	−115.2, p, $J_{bB} = 13.6$, 2.0F
X = N_3 (**2**)	7.22, s, overlap with H6	7,37, d, $J_{45} = 8.1$, H2 + H4 = 1.0H	7.49, t, $J = 7.8$, 1.0H	7.24, d, $J_{56} \approx 8$ Hz, H2 + H6 = 2.0H	66.8, t of 9 lines, $J_{AB} = 150$, $J_{Aa} = 5.1$, 1.0F	45.7, skewed d-m, 4.1F	−97.3, p-d, $J_{Aa} \approx 5.1$, $J_{aB} = 15.0$, 2.0F	−113.7, p, $J_{bB} = 15.0$, 2.0F
X = $CH{=}CH_2$ (**5**)	7.608, s, overlap with H6	7.49, d, overlap with H5, J ≈ 8Hz	7.46, t, $J = 7.8$ Hz, H4 + H5 = 2.0H	7.615, d, $J \approx 8$ Hz, H2 + H6 = 2.0H	67.6, t of 9 lines, $J_{AB} = 151$, $J_{Aa} \approx 4.9$, 1.0F	45.8, skewed d-m, 4.1F	−95.3, p-d, $J_{Aa} \approx 4.9$, $J_{aB} = 14.5$, 2.0F	−114.1, p, $J_{bB} = 14.5$, 2.0F
Vinyl: β′ trans to α	$\delta_\alpha = 6.75$, d-d, $J_{\alpha\beta'} = 17.6$ Hz, $J_{\alpha\beta} = 10.55$ Hz, 1.0H; $\delta_\beta = 5.38$, d, $J = 10.55$ Hz, 1.0H; $\delta_{\beta'} = 5.83$, d, $J = 17.6$ Hz, 1.0H							
X = CH_2CHCOO (**4**)	7.41, s, overlap with H6	7.50, d, $J_{45} = 7.8$ Hz, 1.0H	7.55, t, $J = 8.0$ Hz, 1.0H	7.40, dm, $J \approx 8.2$ Hz, H2 + H6 = 2.0H	64.7, t of 9 lines, $J_{AB} = 150$, $J_{Aa} = 4.9$, 1.0F	45.5, skewed d-m, 3.9F	−95.9, p-d, $J_{Aa} \approx 4.9$, $J_{bB} \approx 14.1$, 2.0F	−113.6, p, $J_{Bb} \approx 14$, 2.0F
Vinyl: β′ trans to α	$\delta_\alpha = 6.33$, d-d, $J_{\alpha\beta'} = 17.\ 7$ Hz, $J_{\alpha\beta} = 10.55$ Hz, 1.0H; $\delta_\beta = 6.07$, d-d, $J = 10.55$ Hz, $J_{\beta\beta'} = 1.15$ Hz, 1.0H; $\delta_{\beta'} = 6.64$, d-d, $J = 17.7$ Hz, $J = 1.15$ Hz, 1.0H							

^{1}H-NMR spectra at 500 MHz, solvent $CDCl_3$, $Si(CH_3)_4$ (internal) = 0, ^{19}F-NMR spectra at 84.7 MHz, solvent $CDCl_3$, CCl_3F (internal) = 0.

for ^{19}F and a GE 500 MHz spectrometer for ^{1}H. The standards $CFCl_3$ (CFC-11) and $(CH_3)_4Si$ were used in the $CDCl_3$ solvent.

Mass spectra were obtained using a Hewlett-Packard HP5890 series II gas chromatograph equipped with a HP5970 mass selective detector operated at 70 eV and a 30 m DB-5 column. For a standard run, the column was maintained at 50 °C for 2 min, followed by an increase in temperature of 11 °C/min until the temperature of the column reached 280 °C. The precise molecular weight determination for compounds (**2–5**) were obtained on a Kratos MS 50TC; chemical ionization with methane.

3.1. Preparation of $SF_5(CF_2)_2C_6H_5$ (*1*)

Into a Parr Bomb (300 ml, series 4560 bench-top minireactor with series 4840 temperature controller) was added $SF_5CF_2CF_2I$ (30.0 g, 0.085 mol) and benzene (175.7 g, 2.2 mol, 26:1 molar ratio). The Parr Bomb was sealed, cooled to −196 °C, evacuated and then charged at room temperature to 3 atm pressure with argon. The reaction mixture was gradually heated (22 °C to 145 °C, 4 h) and stirred (100 rpm); it was then heated at 145 °C for 14 days. The bomb was cooled to room temperature and vented. The dark blue/black liquid was twice distilled with a spinning band distillation system (B/R Instrument Corp., 800 Microsystem). The pot fractions were combined and washed with a 10% aqueous solution of sodium sulfite, a saturated sodium bicarbonate solution, water and then dried over $MgSO_4$. The dried fractions were filtered; the solid residues were washed with 2 ml of CH_2Cl_2. Distillation under reduced pressure gave 19.74 g (0.064 mol) of the product; (**1**) bp 85–87 °C/44 Torr, 74.4% yield. The IR, ^{19}F NMR, and GC-MS data agreed with published values [9].

3.2. Preparation of m-$SF_5CF_2CF_2C_6H_4N_3$ (*2*)

m-$SF_5CF_2CF_2C_6H_4NH_2$ (1.0 g, 3.13 mmol) was diazotized [11]; 0.22 g of NaN_3 in 0.35 ml of water was added dropwise (below 5 °C). The reaction mixture was stirred for 30 min at 0 °C, 1 h at 20 °C and then added to 300 ml of ice-water; the product was extracted 6×, with 75 ml aliquots of ether. Distillation of the evaporated residue obtained from the combined ether fractions gave a clear liquid of *m*-$SF_5CF_2CF_2C_6H_4N_3$ (0.50 g, 1.45 mmol) boiling at 70 °C/0.5 Torr in 46% yield.

3.3. Preparation of m-$SF_5CF_2CF_2C_6H_4Br$ (*3*)

Into a 50 ml round-bottomed flask with a Teflon coated stirring bar and containing 4.96 g (16.3 mmol) of (**1**), 8.2 ml of $CF_3C(O)OH$ and 2.5 ml of conc. H_2SO_4 were added [13]. An air condenser was attached and over an 8 h period, 3.05 g of *N*-bromosuccinimide (1.05 equivalent) was added in small portions; the solution turned a deep orange-red color during the addition. The reaction mixture was added to 200 g of ice water; extracted with CH_2Cl_2 (6×, 50 ml); distillation gave a product boiling at 93–95 °C/15 Torr; 2.31 g (6.03 mmol) in 37% yield.

3.4. Preparation of m-$SF_5(CF_2)_2C_6H_4OC(O)CH{=}CH_2$ (*4*)

To a 50 ml round bottomed flask containing a Teflon stirring bar, 1.20 g (3.75 mmol) of *m*-$SF_5(CF_2)_2C_6H_4OH$ and 25 ml of CH_2Cl_2 were added. The mixture was cooled to −78 °C and acryloyl chloride (0.390 g, 4.31 mmol) in 5 ml of CH_2Cl_2 was added followed by the dropwise addition of a solution of triethylamine (0.400 g, 3.95 mmol in 5 ml CH_2Cl_2). The reaction mixture was warmed to room temperature over a 3 h period. Since the analysis via GC-MS showed that the reaction was not complete, an additional 0.5 ml of acryloyl chloride followed by 1 ml of triethylamine were added (3 h). After removing the solvent, the mixture was washed with water and extracted with CH_2Cl_2 (2× 25 ml); CH_2Cl_2 was removed giving a clear brown liquid. A pure orange oily product, (**4**), (1.33 g) was obtained by column chromatography (20 g silica gel and 1:1 hexane/CH_2Cl_2). The yield of the reaction was 95%.

3.5. Preparation of m-$SF_5(CF_2)_2C_6H_4CH{=}CH_2$ (*5*)

Into a cylindrical Pyrex-glass reaction vessel (30 ml) and equipped with a Teflon stirring bar, *m*-$SF_5(CF_2)_2C_6H_4Br$ (0.320 g, 0.836 mmol), Pd $(P\phi_3)_4$ (19 mg, 0.016 mmol), $(n\text{-}C_4H_9)_3SnCH{=}CH_2$ (0.29 g, 0.90 mmol), and 3 ml toluene were added [12]. The mixture was heated to reflux and stirred for 21 h; since the reaction was not complete, additional $Pd(P\phi_3)_4$ (50 mg) and $(n\text{-}C_4H_9)_3SnCH{=}CH_2$ (11 drops) were added. The mixture was heated to reflux with stirring for 3 h. The solvent was removed under vacuum and the residue was passed through a column chromatography unit containing 20 g silica gel; hexane was used as the solvent. The combined middle fractions were passed through a fresh column; the middle fractions contained the pure styrene product; 0.126 g (0.382 mmol), with a yield of 45.7%.

3.6. Preparation of polyacrylate (*6*)

To a 50 ml Quartz reaction vessel equipped with a Teflon stirring bar and a Kontes Teflon stopcock, 0.480 g (1.28 mmol) of (**4**), (0.02 g) of *tert*-butyl peroxide, and 0.82 g of benzene were added. After degassing, the mixture was heated for 4 days at 93–102 °C. The benzene solvent was removed leaving behind a light yellow solid polymer (0.40 g, 1.07 mmol); yield of 83.6%. The polymer appeared to melt in the 60–70 °C range and decomposed when heated to 255 °C.

The IR spectrum contains the following peaks (cm^{-1}): 3084 (w), 2936 (w), 1761 (w-m), 1596 (w-m), 1491 (w-m), 1448 (m), 1296 (m), 1275 (m-s), 1244 (m), 1202 (s), 1159 (m-s), 1143 (m-s), 1117 (s), 876 (vs), 803 (s), 766 (s), 711 (w-m), 676 (m-s), 608 (s-vs), 574 (s).

*3.7. Preparation of polystyrene (**7**)*

To a 15 ml Pyrex-glass vessel equipped with a Young Teflon stopcock, 0.09 g (0.273 mmol) of (**5**), 0.02 g of *tert*-butyl peroxide, and 0.68 g of benzene were added. After degassing, the reaction mixture was heated at 104–120 °C for 5 days. The benzene was removed leaving behind a clear polymeric material, 0.07 g (0.212 mmol); the yield of polymer was 77.7%. The polymer appears to begin melting in the 70–90 °C range; no decomposition was evident up to 300 °C.

The IR spectrum contained the following peaks (cm^{-1}): 3077 (vw), 3043 (vw), 2929 (w-m), 2853 (w), 1490 (w), 1447 (w-m), 1284 (m-s), 1265 (m), 1243 (w-m) 1196 (vs), 1157 (s), 1116 (vs), 1077 (w-m), 1045 (w), 1003 (vw), 959 (vw), 933 (vw), 875 (vs), 828 (vs), 808 (s), 786 (m), 756 (vs), 707 (m), 697 (w-m), 680 (s), 661 (m), 604 (s), 574 (vs).

Acknowledgements

We are grateful to the National Science Foundation (CHE-9904316) and the Petroleum Research Foundation (ACS-PRF No. 34624-AC7) for support of this work.

References

[1] H.L. Roberts, Quart. Rev. Chem. Soc. 15 (1961) 30.
[2] R. Winter, G.L. Gard, in: J.S. Thrasher, S.H. Strauss (Eds.), Proceedings of the ACS Symposium Series, Vol. 555, 1994, p. 128.
[3] R.D. Verma, R.L. Kirchmeier, J.M. Shreeve, Adv. Inorg. Chem. 41 (1994) 125.
[4] K. Seppelt, D. Lentz, SF_5 Compounds of Carbon, Vol. 295, Wiley, New York, 1997.
[5] R. Winter, P.G. Nixon, G.L. Gard, D.G. Castner, N.R. Holcomb, Y.-H. Hu, D.W. Grainger, Chem. Mater. 11 (1999) 3044.
[6] P.G. Nixon, R. Winter, D.G. Castner, N.R. Holcomb, D.W. Grainger, G.L. Gard, Chem. Mater. 12 (2000) 3108.
[7] R.W. Winter, P.G. Nixon, R.J. Terjeson, J. Mohtasham, N.R. Holcomb, D.W. Grainger, D. Graham, D.G. Castner, G.L. Gard, J. Fluorine Chem., in press.
[8] T.L. St. Clair, A.K. St. Clair, J.S. Thrasher, US Patent 5,220,070 (1993).
[9] S.C. Stinson, Chem. Eng. News 78-28 (2000) 63.
[10] A.M. Hodges, R. Winter, J. Mohtasham, P. Bailey, G.L. Gard, J. Fluorine Chem. 110 (2001) 1.
[11] A.M. Hodges, R.W. Winter, S.W. Winner, D.A. Preston, G.L. Gard, J. Fluorine Chem. 114 (2002) 3.
[12] D.R. McKean, G. Parrinello, A.F. Reanaldo, J.K. Stille, J. Org. Chem. 52 (1987) 422.
[13] J. Duan, L.H. Zhang, W.R. Dolbier, Synletter, 1999, 1245.
[14] C.S. Marvel, C.G. Overberger, R.E. Allen, J.H. Saunders, J. Am. Chem. Soc. 68 (1946) 736.
[15] H.L. Cross, G. Cushing, H.L. Roberts, Spectrochim. Acta 17 (1961) 344.
[16] J.K. Brown, K.J. Morgan, Adv. Fluorine Chem. 4 (1965) 258.
[17] A.L. Logothetis, J. Org. Chem. 29 (1964) 3049.