Synthesis and styrene copolymerization of novel halogen, methyl, and phenoxy ring-disubstituted tert-butyl phenylcyanoacrylates

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Abstract

Novel ring-disubstituted tert-butyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2C(CH_3)_3$, where R is 2-chloro-6-methyl, 3-chloro-4-methyl, 2-fluoro-5-methyl, 2-fluoro-6-methyl, 3-fluoro-2-methyl, 3-fluoro-4-methyl, 4-fluoro-2-methyl, 4-fluoro-3-methyl, 5-fluoro-2-methyl, 4-fluoro-3-phenoxy, were prepared and copolymerized with styrene. The acrylates were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-disubstituted benzaldehydes and tret-butyl cyanoacetate, and characterized by CHN analysis, IR, ^1H and ^{13}C NMR. All the acrylates were copolymerized with styrene in solution with radical initiation at 70°C. The compositions of the copolymers were calculated from nitrogen analysis.

Introduction

3-Chloro-4-methylphenyl propyl [1], and butyl [2] phenylcyanoacrylates (PCA) are synthesized and copolymerized with ethynyl benzene. 4-Fluoro-2-methylphenyl 1-methylethyl [3], and 2-methylpropyl [4] PCAs are prepared and copolymerized with styrene. 4-Fluoro-3-phenoxyphenyl methyl [5], ethyl [6], propyl [7], and 1-methylethyl [8], similarly to 4-chlorophenoxy)phenyl 1,1-dimethylethyl [9], 4-(4-fluorophenoxy) phenyl] butyl [10], and 3-phenoxyphenyl 1,1-dimethylethyl [11] PCAs are used as comonomers in radical copolymerization. 1-[[4-(1,1-Dimethylethyl)-1-cyclohexen-1-yl] oxy]-2-fluorobenzene was mentioned in review of methods to prepare enol ethers [12]; in review of methods to prepare alkyl aryl ethers by substitution [13], and in palladium-catalyzed aryl enol ether synthesis from vinyl triflates [14]. 2-Iodo-5,5-dimethyl-3-phenoxy-2-cyclohexen-1-one is reported in support-free Pd_3Co NCs as an efficient heterogeneous nanocatalyst for new organic transformations of C-C coupling reactions [15]; in iodonium ylide-based three-component reaction leading to 2-spiro-substituted dihydrofurans [16]; in synthesis and structural characterization of Cu(I) complexes with the antithyroid drug 6-n-propyl-thiouracil and intermolecular cycloaddition of iodonium ylides toward benzo[b]furans with pharmaceutical implementations [17]; in preparation of dimedone-derived iodonium ylides and their reaction with carbodiimide leading to oxazole derivatives [18], and [3+2]-cycloaddition reactions of 2-phenyliodonio-5,5-dimethyl-1,3-dioxacyclohexanemethylide [19]. In this work we have prepared novel ring-disubstituted tert-butyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2C(CH_3)_3$, where R is 2-chloro-6-methyl, 3-chloro-4-methyl, 2-fluoro-5-methyl, 2-fluoro-6-methyl, 3-

fluoro-2-methyl, 3-fluoro-4-methyl, 4-fluoro-2-methyl, 4-fluoro-3-methyl, 5-fluoro-2-methyl, 4-fluoro-3-phenoxy, and explored the feasibility of their copolymerization with styrene. To the best of our knowledge there have been no reports on either synthesis of these compounds, nor their copolymerization with styrene [20].

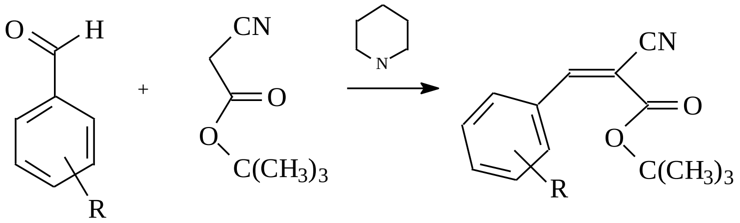
2. Experimental

2-Chloro-6-methyl, 3-chloro-4-methyl, 2-fluoro-5-methyl, 2-fluoro-6-methyl, 3-fluoro-2-methyl, 3-fluoro-4-methyl, 4-fluoro-2-methyl, 4-fluoro-3-methyl, 5-fluoro-2-methyl, 4-fluoro-3-phenoxy benzaldehydes, tert-butyl cyanoacetate (≥98.0%), piperidine (99%), styrene (≥99%), 1,1'-azobis(cyclohexanecarbonitrile) (98%), (ABCN), and toluene (98%) supplied from Sigma-Aldrich Co., were used as received. Instrumentation was reported in [21].

3. Results and discussion

3.1. Synthesis and characterization of tert-butyl phenylcyanoacrylates

All tert-butyl phenylcyanoacrylates (TBCA) compounds were synthesized by Knoevenagel condensation [22] of appropriate benzaldehydes with tert-butyl cyanoacetate, catalyzed piperidine (Scheme 1).



Scheme 1. Synthesis of tert-butyl phenylcyanoacrylates where R is 2-chloro-6-methyl, 3-chloro-4-methyl, 2-fluoro-5-methyl, 2-fluoro-6-methyl, 3-fluoro-2-methyl, 3-fluoro-4-methyl, 4-fluoro-2-methyl, 4-fluoro-3-methyl, 5-fluoro-2-methyl, 4-fluoro-3-phenoxy.

The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of tert-butyl cyanoacetate and an appropriate benzaldehyde were mixed in equimolar ratio in a 20 mL vial. A few drops of piperidine were added with stirring. The product of the reaction was isolated by filtration and purified by crystallization from 2-propanol. The compounds were characterized by IR, ^{1}H and ^{13}C NMR, and elemental analysis. No stereochemical analysis of the novel compounds was performed since no stereoisomers (*E* or/and *Z*) of known configuration were available.

3.1.1. *Tert-butyl 2-chloro-6-methylphenylcyanoacrylate*

Yield 63%; ^{1}H NMR δ 8.3 (s, 1H, CH=), 7.3-6.9 (m, 3H, Ph), 2.4 (s, 3H, $PhCH_3$), 1.6 (s, 9H, CH_3); ^{13}C NMR δ 159 (C=O), 154 (HC=), 138, 133, 131, 129, 127, 114 (Ph), 115 (CN), 114 (C=), 84 (OC), 28 (CH_3), 20 (CH_3); IR (cm^{-1}): 2953 (m, C-H), 2224 (m, CN), 1726 (s, C=O), 1645 (s, C=C), 1284 (s, C-O-CH_3), 783 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{16}ClNO_2$: C, 64.87; H, 5.81; N, 5.04; Found: C, 64.44; H, 6.17; N, 5.39.

3.1.2. Tert-butyl 3-chloro-4-methylphenylcyanoacrylate

Yield 78.5%; mp 74.1°C; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.9-7.1 (m, 3H, Ph), 2.5 (s, 3H, $PhCH_3$), 1.6 (s, 9H, CH_3); ^{13}C NMR δ 161 (C=O), 150 (HC=), 141, 135, 132, 130, 127, 115 (Ph), 117 (CN), 105 (C=), 84 (OC), 28 (CH_3), 21 (CH_3); IR (cm^{-1}): 2982 (m, C-H), 2224 (m, CN), 1724 (s, C=O), 1610 (s, C=C), 1296 (s, C-O-CH_3), 843 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{16}ClNO_2$: C, 64.87; H, 5.81; N, 5.04; Found: C, 64.09; H, 5.81; N, 4.84.

3.1.3. Tert-butyl 2-fluoro-5-methylphenylcyanoacrylate

Yield 72%; ^{1}H NMR δ 8.5 (s, 1H, CH=), 8.3-6.8 (m, 3H, Ph), 3.9 (s, 3H, PhCH_3), 1.6 (s, 9H, CH_3); ^{13}C NMR δ 161 (C=O), 157 (HC=), 147, 138, 137, 130, 127, 112 (Ph), 116 (CN), 106 (C=), 84 (OC), 28 (CH_3), 21 (CCH_3); IR (cm^{-1}): 2982 (m, C-H), 2222 (m, CN), 1726 (s, C=O), 1612 (s, C=C), 1278 (s, C-O-CH_3), 847 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{16}FNO_2$: C, 68.95; H, 6.17; N, 5.36; Found: C, 63.71; H, 5.77; N, 4.27.

3.1.4. Tert-butyl 2-fluoro-6-methylphenylcyanoacrylate

Yield 87%; mp 74.8°C; ^{1}H NMR δ 8.2 (s, 1H, CH=), 7.4-6.9 (m, 3H, Ph), 2.4 (s, 3H, PhCH_3), 1.6 (s, 9H, CH_3); ^{13}C NMR δ 160 (C=O), 149 (HC=), 140, 132, 128, 126, 120, 113 (Ph), 114 (CN), 106 (C=), 84 (OC), 28 (CH_3), 20 (PhCH_3); IR (cm^{-1}): 2997 (m, C-H), 2224 (m, CN), 1715 (s, C=O), 1614 (s, C=C), 1281 (s, C-O-CH_3), 841 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{16}FNO_2$: C, 68.95; H, 6.17; N, 5.36; Found: C, 67.58; H, 6.61; N, 5.81.

3.1.5. *Tert-butyl 3-fluoro-2-methylphenylcyanoacrylate*

Yield 88%; mp 34.1°C; ^{1}H NMR δ 8.4 (s, 1H, CH=), 7.3-6.6 (m, 3H, Ph), 3.8 (s, 3H, PhCH_3), 1.6 (s, 9H, CH_3); ^{13}C NMR δ 162 (C=O), 145 (HC=), 130, 114, 113, 111 (Ph), 116 (CN), 101 (C=), 84 (OC), 28 (CH_3), 23 (PhCH_3); IR (cm^{-1}): 2982 (m, C-H), 2222 (m, CN), 1726 (s, C=O), 1614 (s, C=C), 1242 (s, C-O-CH_3), 848 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{16}FNO_2$: C, 68.95; H, 6.17; N, 5.36; Found: C, 66.79; H, 6.46; N, 5.91.

3.1.6. *Tert-butyl 3-fluoro-4-methylphenylcyanoacrylate*

Yield 91%; mp 101.7°C; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.7-7.0 (m, 3H, Ph), 2.4 (s, 3H, $PhCH_3$), 1.6 (s, 9H, CH_3); ^{13}C NMR δ 162 (C=O), 153 (HC=), 132, 131, 127, 116 (Ph), 117 (CN), 106 (C=), 84 (OC), 28 (CH_3), 15 ($PhCH_3$); IR (cm^{-1}): 2978 (m, C-H), 2226 (m, CN), 1709 (s, C=O), 1610 (s, C=C), 1276 (s, C-O-CH_3), 849 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{16}FNO_2$: C, 68.95; H, 6.17; N, 5.36; Found: C, 68.04; H, 6.27; N, 5.35.

3.1.7. Tert-butyl 4-fluoro-2-methylphenylcyanoacrylate

Yield 97%; ^{1}H NMR δ 8.4 (s, 1H, CH=), 7.9-7.0 (m, 3H, Ph), 2.3 (s, 3H, $PhCH_3$), 1.6 (s, 9H, CH_3); ^{13}C NMR δ 163 (C=O), 153 (HC=), 134, 127, 126, 120, 114, 113 (Ph), 117 (CN), 104 (C=), 84 (OC), 28 (CH_3), 12 ($PhCH_3$); IR (cm^{-1}): 2982 (m, C-H), 2222 (m, CN), 1722 (s, C=O), 1595 (s, C=C), 1288 (s, C-O-CH_3), 845 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{16}FNO_2$: C, 68.95; H, 6.17; N, 5.36; Found: C, 68.80; H, 6.39; N, 6.59.

3.1.8. *Tert-butyl 4-fluoro-3-methylphenylcyanoacrylate*

Yield 97%; ^{1}H NMR δ 8.1 (s, 1H, CH=), 7.9-6.8 (m, 3H, Ph), 2.3 (s, 3H, $PhCH_3$), 1.6 (s, 9H, CH_3); ^{13}C NMR δ 161 (C=O), 152 (HC=), 145, 135, 131, 128, 114 (Ph), 116 (CN), 103 (C=), 84 (OC), 28 (CH_3), 15 ($PhCH_3$); IR (cm^{-1}): 2982 (m, C-H), 2223 (m, CN), 1744 (s, C=O), 1682 (s, C=C), 1250 (s, C-O-CH_3), 842 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{16}FNO_2$: C, 68.95; H, 6.17; N, 5.36; Found: C, 66.54; H, 6.59; N, 6.08.

3.1.9. *Tert-butyl 5-fluoro-2-methylphenylcyanoacrylate*

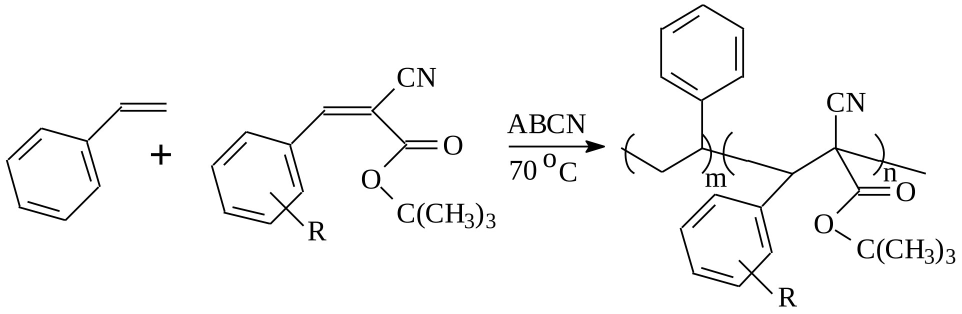
Yield 97%; mp 73.5°C; ^{1}H NMR δ 8.4 (s, 1H, CH=), 7.9-7.0 (m, 3H, Ph), 2.4 (s, 3H, PhCH$_3$), 1.6 (s, 9H, CH$_3$); ^{13}C NMR δ 161 (C=O), 150 (HC=), 137, 131, 119, 116 (Ph), 117 (CN), 103 (C=), 84 (OC), 28 (CH$_3$), 16 (PhCH$_3$); IR (cm^{-1}): 2982 (m, C-H), 2244 (m, CN), 1722 (s, C=O), 1612 (s, C=C), 1242 (s, C-O-CH$_3$), 856 (s, C-H out of plane). Anal. Calcd. for $C_{15}H_{16}FNO_2$: C, 68.95; H, 6.17; N, 5.36; Found: C, 68.06; H, 6.78; N, 6.03.

3.1.10. *Tert-butyl 4-fluoro-3-phenoxyphenylcyanoacrylate*

Yield 98%; mp 150.3°C; ^{1}H NMR δ 8.0 (s, 1H, CH=), 7.9-6.9 (m, 8H, Ph), 1.6 (s, 9H, CH$_3$); ^{13}C NMR δ 162 (C=O), 153 (HC=), 152, 130, 129, 128, 125, 118 (Ph), 117 (CN), 103 (C=), 84 (OC), 28 (CH$_3$); IR (cm^{-1}): 2985 (m, C-H), 2222 (m, CN), 1744 (s, C=O), 1510 (s, C=C), 1275 (s, C-O-CH$_3$), 849 (s, C-H out of plane). Anal. Calcd. for $C_{20}H_{18}FNO_3$: C, 70.78; H, 5.35; N, 4.13; Found: C, 68.08; H, 5.87; N, 5.10.

3.3. *Synthesis and characterization of styrene – TPCA copolymers*

Copolymers of the ST and the TBCA compounds, P(ST-co-TBCA) were prepared in 25-mL glass screw cap vials at ST/TBCA = 3 (mol) the monomer feed using 0.12 mol/L of ABCN at an overall monomer concentration 2.44 mol/L in 10 mL of toluene. The copolymerization was conducted at 70ºC. After a predetermined time, the mixture was cooled to room temperature, and precipitated dropwise in methanol. The composition of the copolymers was determined based on the nitrogen content (cyano group in TBCA). The novel synthesized TBCA compounds copolymerized readily with ST under free-radical conditions (Scheme 2) forming white flaky precipitates when their solutions were poured into methanol. The conversion of the copolymers was kept between 10 and 20% to minimize compositional drift (Table 1).



Scheme 2. Copolymerization of ST and the tert-butyl phenylcyanoacrylates, where R is 2-chloro-6-methyl, 3-chloro-4-methyl, 2-fluoro-5-methyl, 2-fluoro-6-methyl, 3-fluoro-2-methyl, 3-fluoro-4-methyl, 4-fluoro-2-methyl, 4-fluoro-3-methyl, 5-fluoro-2-methyl, 4-fluoro-3-phenoxy.

Table 1. Copolymerization of styrene and tert-butyl phenylcyanoacrylates.

R	Yield[a] (wt%)	N (wt%)	ST in copol. (mol%)	TBCA in copol. (mol%)
2-Chloro-6-methyl	11.2	1.19	89.6	10.4
3-Chloro-4-methyl	13.3	1.9	81.5	18.5
2-Fluoro-5-methyl	14.4	2.41	75.5	24.5
2-Fluoro-6-methyl	11.2	1.87	82.4	17.6
3-Fluoro-2-methyl	15.2	2.25	77.6	22.4
3-Fluoro-4-methyl	13.1	2.49	74.3	25.7
4-Fluoro-2-methyl	11.7	2.27	77.4	22.6
4-Fluoro-3-methyl	15.2	1.75	83.8	16.2
5-Fluoro-2-methyl	13.2	1.57	85.8	14.2
4-Fluoro-3-phenoxy	11.9	2.33	76.6	23.4

Nitrogen elemental analysis showed that between 10.4 and 25.7 mol% of TBCA is present in the copolymers prepared at ST/ TBCA = 3 (mol), which is indicative of relatively high reactivity of the TBCA monomers towards ST radical which is typical of alkoxy ring-substituted TBCA. Since TBCA monomers do not homopolymerize, the most likely structure of the copolymers would be isolated TBCA monomer units alternating with short ST sequences (Scheme 2).

The copolymers prepared in the present work are all soluble in ethyl acetate, THF, DMF and $CHCl_3$ and insoluble in methanol, ethyl ether, and petroleum ether.

4 Conclusions

Novel trisubstituted ethylenes, tert-butyl phenylcyanoacrylates, $RPhCH=C(CN)CO_2C(CH_3)_3$ (where R is 2-chloro-6-methyl, 3-chloro-4-methyl, 2-fluoro-5-methyl, 2-fluoro-6-methyl, 3-fluoro-2-methyl, 3-fluoro-4-methyl, 4-fluoro-2-methyl, 4-fluoro-3-methyl, 5-fluoro-2-methyl, 4-fluoro-3-phenoxy were prepared and copolymerized with styrene.

Acknowledgments

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