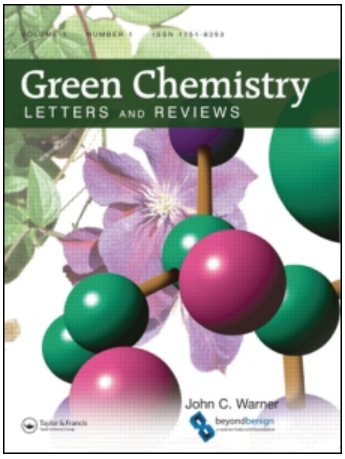

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ORIGINAL ARTICLE

Aryl ethyl ethers prepared by ethylation using diethyl carbonate

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An environmentally more convenient reaction for the production of industrially important aryl ethyl ethers (ArOEts) is described. ArOEts were selectively obtained in essentially quantitative yields by the reaction of corresponding (hetero)aromatic alcohols (ArOHs) with diethyl carbonate as the environmentally friendly alkylating reagent in the presence of *N,N*-dimethylacetamide used as polar aprotic cosolvent, and sodium ethoxide as the base. The reactions were carried out in the air under atmospheric pressure at 137°C. Reaction equilibrium was shifted by distilling the ethanol from the reaction mixture. All ArOEts were isolated by evaporation of the reaction mixture, and subsequent extraction with water and diethoxymethane. The ethylation agent and used solvents were non-toxic, recyclable and biologically degradable. Wastewater from the extraction was successfully treated by Fenton oxidation and returned to the next work-up process.

Keywords: Ethylation; diethyl carbonate; phenols; aryl ethyl ethers

Introduction

Aryl ethyl ethers (ArOEts) are a useful source in the preparation of dyes (e.g., Algol orange RF), fragrances (e.g., naphtyl ethyl ether), pharmaceuticals (e.g., analgesic Phenacetin, anesthetic Parethoxycaine), and in many other valuable by-products (*1*). The most common method of production is the *O*-ethylation of phenols with diethyl sulphate (*2*) or ethyl halides (*3*). These reagents are toxic and environmentally problematic. The disadvantages of ethyl halides include handling under elevated pressure and their surplus due to low boiling points. Ethyl esters of organic sulphonic acids (*4*) are, in some cases, also useful reagents, but production and disposal of unrecyclable stoichiometric amounts of corresponding alkali metal salts are a major drawback of such a method. These toxic and waste producing reagents have a valuable green alternative in diethyl carbonate (DEC). Many of the properties of DEC make it a genuinely green reagent. DEC is a non-toxic compound (*5*). Among the specific advantages of DEC are that its building blocks are CO_2 and ethanol, environmentally benign compounds, which do not cause emissions of volatile organic compounds (VOCs) into the atmosphere. Symmetrical dialkyl carbonates are also cost-effective reagents. Dimethyl carbonate (DMC) is the best-screened dialkyl carbonate for alkylation of phenols (*6–16*). However, a major operative drawback of DMC-mediated alkylation is determined by the reaction temperature (between 120 and 200°C), which is higher than the boiling point of DMC (90°C). Basic zeolites (*6*), aluminas or alumina-silica (*7*) were described as catalysts in a continuous-flow process at temperatures of 160–300°C in the vapor phase, but *C*-methylated by-products are often formed, and this procedure is not suitable for phenols with a high boiling point. The *O*-methylation of phenols can be carried out in a pressure reactor at a temperature above 160°C in the presence of alkali (K_2CO_3 (*8*), Cs_2CO_3 (*9*)) or organic bases (tertiary amines (*10*), phosphines (*11*), pentaalkylguanidines (*12*)). In most cases, *N,N*-dimethylformamide is used as the cosolvent. However, this polar aprotic solvent is toxic and unstable under higher temperature, especially in an alkaline medium. Under atmospheric pressure, an efficient batch synthesis of aryl methyl ethers has been developed in the presence of K_2CO_3-crown ether (*7*), K_2CO_3–Bu_4NBr (*13*) or DBU (*14*). However, an obvious disadvantage is the difficulty of recovering and recycling the homogeneous catalyst.

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Shen et al. published a method in which methylation of phenols with DMC was achieved at 120°C under atmospheric pressure in ionic liquid (*15*). Due to their high boiling points, asymmetric alkyl methyl carbonates have been tested to accomplish *O*-methylation under an atmospheric pressure between 120 and 150°C in the presence of K_2CO_3 and triglyme or DMF as a polar solvent (*16*).

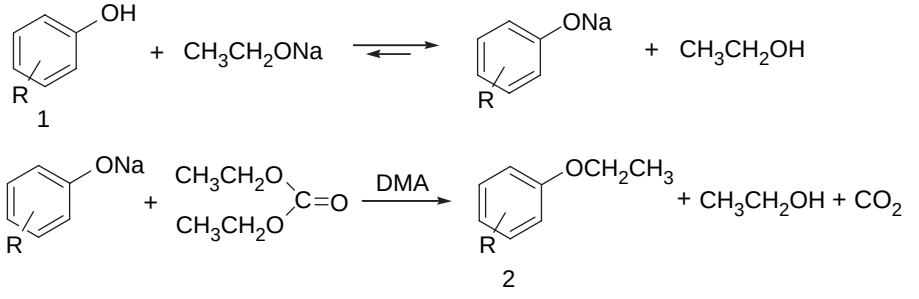
O-ethylation using DEC is an unexplored area. Tundo (*17*) published that the reaction rate of alkylation using higher homologues of dialkyl carbonates embodies a decrease under the same reaction conditions compared to DMC. In the case of phenol, *O*-alkylation with ethyl methyl carbonate proceeds in the molar ratio 9:1 for methyl versus ethyl ether. It appears that such selectivity can be easily explained by steric factors (*18*). On the other hand, the boiling point of DEC is 125°C, which might enable alkylation under atmospheric pressure. Ouk et al. (*8*) reported only two examples of efficient *O*-ethylation of *p*-cresol and phenol using special equipment. However, the complete conversion of substrates cannot be achieved.

In this paper, we focused our attention on a Williamson type synthesis of ArOEts using DEC as an alternative and environmentally more suitable alkylation agent.

Results and discussion

The reaction permitting the *O*-ethylation of **1** using DEC under atmospheric pressure with essentially quantitative conversion to **2** has been reported (Scheme 1, Table 1). We verified that ethylation of the phenols using DEC without the addition of polar aprotic solvent failed. *N,N*-Dimethylacetamide (DMA) was used as a low toxicity polar solvent instead of the thermally unstable and more toxic DMF (*5*). A solution of sodium ethylate in ethanol was chosen as a strong and cheap base to activate phenol by deprotonation. After evaporation to dryness under reduced pressure, the reaction mixture was cooled to room temperature. Subsequently, a small quantity of water was added and extracted with methylal (dimethoxymethane) or ethylal (diethoxymethane). It has been published that ethylal is a potential replacement for dichloromethane for phase-transfer catalyzed reactions (*19*). We proved in this work that methylal or ethylal are better solvents than dichloromethane for the isolation of formed ArOEts not only for environmental reasons (see Table 2). Both acetals have lower densities than water, and emulsions are not formed during the extraction of alkaline water solutions of evaporated reaction mixture. An advantage of ethylal is the higher boiling point (87.5°C). The loss of ethylal during the recycling procedure (distillation) is much lower (maximum 10%) than the loss of methylal (around 30%).

In the starting experiments, **1a** was used to find sufficient reaction conditions for essentially quantitative ethylation. We verified that dropwise addition of 2 M sodium ethylate to the solution of **1a** in DMA and DEC at 90–100°C is the best method to avoid sudden thickening of the reaction mixture. The temperature of the reaction mixture was increased progressively from 90 to 137°C by continuous distillation of ethanol. When distillation of EtOH was finished, a thin slurry was formed. The composition of the reaction mixture was analyzed by ^{1}H NMR spectroscopy after evaporation of a sample in vacuo to dryness. After 24 h of heating at 137°, residues of unreacted **1a** were present in the reaction mixture. After an additional day of heating at 137°C, the *O*-ethylation of **1a** was completed with quantitative conversion to **2a**. Following these conditions, other phenols have also been tested. Complete ethylation of one equivalent of OH group involves 1.2 equivalents of NaOEt (see Table 1). It was observed that hydroxybenzoic acids **1j** and **1k** are converted to the corresponding ethyl ethoxybenzoates **2j** and **2k** under the above-mentioned reaction conditions (see Table 1, entry 10 and 11). In the case of using catalytic amounts of NaOEt, low conversion of the starting



Scheme 1. Ethylation of ArOH using DEC.

Table 1. Synthesis of aryl ethyl ethers using DEC.

Entry	Starting Ar–OH	Excess of EtONa based on ArOH	Reaction conditions	Obtained product	Yield of isolated ArOEt (%)	Molecular formula of ArOEt	Calculated/found:%C,%H
1	2-Naphtol **1a**	1.2 eq	137°C/42 h	2-Ethoxynaphtalene **2a**	96	$C_{12}H_{12}O$ 172.23	83.69; 7.02/83.25; 7.07
2	*m*-Cresol **1b**	1.2 eq	137°C/46 h	1-Ethoxy-3-methylbenzene **2b**	73	$C_9H_{12}O$ 136.19	79.37; 8.88/79.10; 8.93
3	4-Hydroxybiphenyl **1c**	1.2 eq	137°C/45 h	4-Ethoxybiphenyl **2c**	93	$C_{14}H_{14}O$ 198.26	84.81; 7.12/84.54; 7.14
4	8-Hydroxyquinoline **1d**	1.2 eq	137°C/48 h	8-Ethoxyquinoline **2d**	98	$C_{11}H_{11}NO$ 173.21	76.28; 6.40; N: 8.08/76.10; 6.43; N: 7.92
5	2-Nitrophenol **1e**	1.2 eq	137°C/42 h	1-Ethoxy-2-nitrobenzene **2e**	93	$C_8H_9NO_3$ 167.16	57.43; 5.43; N: 8.38/57.81; 5.51; N: 8.20
6	Resorcinol **1f**	1.2 eq	137°C/48 h	1,3-Diethoxybenzene **2f**	90	$C_{10}H_{14}O_2$ 166.22	72.26; 8.49/72.78; 8.59
7	4-Hydroxy-*N,N*-dimethylaniline **1g**	1.2 eq	137°C/47 h	4-Ethoxy-*N,N*dimethylaniline**2g**	90	$C_{10}H_{15}NO$ 165.23	72.69; 9.15; N: 8.48/73.22; 9.23; N: 8.37
8	4-Tert-butyl phenol**1h**	1.2 eq	137°C/42 h	1-Tert-butyl-4-ethoxybenzene **2h**	89	$C_{12}H_{18}O$ 178.27	80.85; 10.18/80.39; 10.21
9	Phenol **1i**	1.2 eq	137°C/42 h	Ethoxybenzene **2i**	71	$C_8H_{10}O$ 122.17	78.65; 8.25/78.53; 8.29
10	4-Hydroxybenzoic acid **1j**	2.2 eq	137°C/45.5 h	4-Ethoxy-benzoic acid ethyl ester **2j**	93	$C_{11}H_{14}O_3$ 194.23	67.96; 7.21/68.19; 7.28
11	Salicylic acid **1k**	2.2 eq	137°C/48 h	2-Ethoxy-benzoic acid ethyl ester **2k**	92	$C_{11}H_{14}O_3$ 194.23	67.96; 7.21/67.37; 7.30
12	2,2-Bis-(4-hydroxyphenyl)-propane **1l**	2 eq	137°C/45 h	2,2-Bis-(4-ethoxyphenyl)propane **2l**	96 (1°); 93 (2°); 94.4 (3°)	$C_{19}H_{24}O_2$ 284.40	80.17; 8.44/79.52; 8.56

Table 2. Comparison between the physical, toxicological and eco-toxicological properties of DEK, ethyl chloride and diethyl sulphate (DES) as applicable ethylating agents, DMF and DMA as applicable polar aprotic solvents and dichloromethane and acetals as applicable extracting agents (*5*,*19*).

Properties	DEC	EtCl	DES	DMA	DMF	CH_2Cl_2	Methylal	Ethylal
Boiling point (°C)	125.0–126.0	12.3	88.0–91.0/1.33 kPa	164.5–166.0	153	40	42.3	85.0–88.0
Oral acute toxicity (rats) LD_{50}	8500 mg/kg	LC_{50}: 146,000 mg/m^3 2 h	880 mg/kg	4300 mg/kg	2800 mg/kg	1600 mg/kg	>7000 mg/kg	2604 mg/kg
Toxicity	Irritant	Deleterious	Toxic	Toxic	Toxic	Deleterious	No	No
Carcinogenic properties	No	Carcinogen group 3	Carcinogen, group 2A	No	No	Suspected carcinogen	No	No

(hetero)aromatic alcohols (ArOHs) was obtained. The use of PEG as a solvent alternative to DMF was described earlier (*17*). The PEG was not tested intentionally in our work because of its high boiling point (which complicated isolation of most of the formed ArOEts and the recycling of PEG was practically disabled). Our attempts to displace the polar aprotic solvent DMA with glycerol formal (commercially available mixture of 5-hydroxy-1,3-dioxane and 4-hydroxymethyl-1,3-dioxolane, b.p. 193°C) led to the formation of a multi-product mixture under the same reaction conditions.

The ethylation of **1l** was run three times consecutively, recycling the reagent (DEC) and solvent (DMA) mixture each time. In the second and third cycles, recycled solvents were used. Gravimetric and ^{1}H NMR analysis of distillates indicated $<3\%$ average loss of DMA, 10% loss of DEK, and 10% loss of ethylal in each reaction cycle. The concentration of DEC relative to DMA was determined by ^{1}H NMR spectroscopy as a ratio of integral values of methyl group signals (1.29 ppm quartet of two CH_3 groups of DEC and 2.08 ppm singlet of CH_3CO group of DMA). The loss of DEC and DMA were supplemented in such a way that the amount and ratio of DEC to DMA was the same as in the first cycle of the ethylation procedure, where pure DEC and DMA from the commercial supplier were used.

The modified version of Fenton oxidation (*20*) was used for wastewater purification.

Experimental

All operations were carried out in the air. All ArOHs, DEC, DMA were purchased from Sigma Aldrich and Merck at a purity of at least 97% and used without further purification. Acetals, glycerol formal, methylal and ethylal were obtained from Lambiotte & Cie S.A. (Belgium) in ultra pure quality and used as received. The solution of sodium ethoxide was prepared by dissolution of pieces of sodium metal in ethanol. The concentration of base was analyzed by a titration method using 1 M HCl and phenolphthalein as the indicator. For vacuum evaporation, the diaphragm pump KNF N816.3.KT18 was used. The synthesized substances were identified by means of their ^{1}H and ^{13}C NMR spectra, elemental analyses and, if applicable, by comparison of their melting points with data in the literature. The ^{1}H and ^{13}C NMR spectra were recorded at 25°C on a Bruker AMX 360 spectrometer at frequencies of 360.14 and 90.57 MHz, respectively. For the measurements, the substances were dissolved in $CDCl_3$. The δ ^{1}H chemical shifts are referenced to the signal of TMS (δ ^{1}H: 0.00). The δ ^{13}C chemical shifts are referenced to the signals of the solvent (δ ^{13}C: 77.0). The signals in the ^{13}C NMR spectra were assigned by means of APT (attached proton test), this method enables differentiation between the resonances of quarternary carbons (C) and carbons of CH, CH_2 and CH_3 groups. In addition, measured NMR spectra of synthesized ArOEts were compared with those published earlier (*21–29*).

The elemental analyses were carried out on an automatic analyzer EA 1108 (Fisons). Melting points were determined on a Boetius (Carl Zeiss Jena) apparatus. TOC and Tnb values were measured on a TOC analyzer liquiTOC furnished with TN module (Elementar Analysensysteme, GmbH, Germany).

The following procedure for preparation of the 2,2-bis-(4-ethoxy-phenyl)-propane **2l** represents the general method used for the synthesis of ArOEts. This procedure was repeated three times with the recycling of solvents and DEC.

2,2-Bis-(4-ethoxy-phenyl)-propane **(2l)**

The reaction was carried out in a 1000-ml, three-necked, round-bottomed flask equipped with magnetic stirring, thermometer, dropping funnel and distillation head and condenser. Outlet of the apparatus was fitted with a calcium chloride trap. The reaction flask was immersed in the oil bath. 2,2-Bis-(4-hydroxy-phenyl)-propane **1l** (17.1 g, 0.075 mol) was dissolved in the mixture of DMA (150 ml, 139.5 g) and DEC (150 ml, 141.7 g). The solution was heated to 80–90°C and 2 M ethanolic solution of sodium ethoxide (120 ml, 0.15 mol) was added dropwise to the mixture. On completion of the addition, the dropping funnel was flushed with 20 ml of ethanol. The temperature of the reaction mixture was raised from 80 to 135°C by continuous distillation of ethanol over a period of approximately 2 h. The final temperature of the reaction mixture, after distillation of most of the ethanol, was maintained at 137°C (at 160°C oil bath) for an additional 2 days. During this time, about 125.8 g (154 ml) of distillate was obtained. This distillate contained 96.5 mol% of ethanol and 3.5 mol% of DEC. The reaction mixture was cooled and the solvents were removed by evaporation under vacuum ($p = 1.6$ kPa by temperature 40–90°C). The distilled mixture 263.3 g (274 ml) was obtained and contained 35.9 mol% of DEC and 64.1 mol% of DMA by ^{1}H NMR analysis. The residue was diluted with 100 ml of water and extracted with ethylal (3×100 ml). The organic extracts were collected, repeatedly extracted with a saturated

aqueous solution of Na_2SO_4 (3×50 ml) and passed through a short column packed with silica gel. The column was washed with 50 ml of ethylal and the filtrated solution was distilled to dryness yielding 21.3 g (96% yield) of solid 2,2-bis-(4-ethoxy-phenyl)-propane **2l**. Mp 48–50°C (lit. (*30*) 48–50°C); δ_H (360.13 MHz, $CDCl_3$) 1.41 (t, 6H), 1.65 (s, 6H), 4.00 (q, 4H), 6.81 (d, 4H), 7.15 (d, 4H); δ_C (90.55 MHz, $CDCl_3$) 14.8 ($2 \times CH_3$), 30.9 ($2 \times CH_3$), 41.5 (C), 63.2 ($2 \times CH_2$), 113.6 (4CH), 127.6 (4CH), 142.9(C), 156.6 (C).

The wastewater (136.5 g, TOC value: 42 525 mg/l, total N: 14 780 mg/l) obtained from the extraction step was saturated with ethylal. Initially, the dissolved ethylal was removed by distillation at 75–99°C. The distillation residue was acidified using an aqueous solution of H_2SO_4 (48 wt%, 20 g), to a pH value of 2.3, and $FeSO_4.7H_2O$ (9.3 g, 0.05 mol) was added. To this solution, H_2O_2 (25 ml, 30 wt%) was added in five 5 ml portions at 5-min intervals under vigorous agitation. The mixture turned brown and a little foam formed. After 30 min of stirring, the reaction mixture was made slightly alkaline (pH = 7.5) using 20 wt% of aqueous NaOH, and the slurry was filtered after 30 min of agitation. Colorless water was obtained (98 g, TOC value 115 mg/l, total N: 41.5 mg/l, COD: 115 mg/l) and used for dilution of the reaction mixture in the next reaction cycle.

The combined saturated solutions of Na_2SO_4 were extracted with three 50 ml portions of ethylal and the extracted Na_2SO_4 solution was used for extraction in the next cycle. The combined ethylal extracts (containing DMA) obtained in this step were used for the extraction of the product in the next cycle without purification.

2-Ethoxynaphtalene **2a**
m.p. 36–38°C (lit. (*31*) 37–38°C); δ_H (360.13 MHz, $CDCl_3$) 1.46 (t, 3H), 4.11 (q, 2H), 7.12 (m, 2H), 7.31 (m, 1H), 7.42 (m, 1H), 7.72 (m, 3H); δ_C (90.55 MHz, $CDCl_3$) 14.7 (CH_3), 63.3 (CH_2), 106.4 (CH), 118.9 (CH), 123.4 (CH), 126.2 (CH), 126.6 (CH), 127.5 (CH), 128.8 (C), 129.2 (CH), 134.5 (C), 156.8 (C).

1-Ethoxy-3-methylbenzene **2b**
Obtained in 73% yield as an oil. δ_H (360.13 MHz, $CDCl_3$) 1.37 (t, 3H), 2.29 (s, 3H), 3.95 (q, 2H), 6.70 (m, 3H), 7.12 (t, 1H); δ_C (90.55 MHz, $CDCl_3$) 14.7 (CH_3), 21.3 (CH_3), 62.9 (CH_2), 111.1 (CH), 115.1 (CH), 121.1 (2CH), 129.0 (CH), 139.1 (C), 158.8 (C).

4-Ethoxybiphenyl **2c**
Obtained in 93% yield as a solid. m.p.: 73–75°C (lit. (*32*) 76°C); δ_H (360.13 MHz, $CDCl_3$) 1.41 (t, 3H), 4.02 (q, 2H), 6.94 (d, 2H), 7.28 (t, 1H), 7.39 (t, 2H), 7.53 (m, 3H); δ_C (90.55 MHz, $CDCl_3$) 14.8 (CH_3), 63.4 (CH_2), 114.7 (CH), 126.5 (2CH), 126.6 (2CH), 128.0 (2CH), 128.6 (2CH), 133.5 (C), 140.8 (C), 158.4 (C).

8-Ethoxyquinoline **2d**
Obtained in 98% yield as an oil. δ_H (360.13 MHz, $CDCl_3$) 1.63 (t, 3H), 4.29 (q, 2H), 7.02 (d, 1H), 7.37 (m, 3H), 8.08 (d, 1H), 8.93 (m, 1H); δ_C (90.55 MHz, $CDCl_3$) 14.4 (CH_3), 63.9 (CH_2), 108.1 (CH), 119.0 (CH), 121.2 (CH), 126.4 (CH), 129.1 (C), 135.6 (CH), 139.9 (C), 148.9 (CH), 154.3 (C).

1-Ethoxy-2-nitrobenzene **2e**
Obtained in 93% yield as an oil. δ_H (360.13 MHz, $CDCl_3$) 1.40 (t, 3H), 4.14 (q, 2H), 6.95 (t, 1H), 7.04 (d, 1H), 7.46 (t, 1H), 7.72 (d, 1H); δ_C (90.55 MHz, $CDCl_3$) 14.1 (CH_3), 65.0 (CH_2), 114.3 (CH), 119.8 (CH), 125.0 (CH), 133.8 (CH), 139.6 (C), 151.9 (C).

1,3-Diethoxybenzene **2f**
Obtained in 90% yield as an oil. δ_H (360.13 MHz, $CDCl_3$) 1.40 (t, 6H), 4.01 (q, 4H), 6.48 (m, 3H), 7.16 (t, 1H); δ_C (90.55 MHz, $CDCl_3$) 14.7 ($2CH_3$), 63.3 ($2CH_2$), 101.3 (CH), 106.6 (2CH), 129.7 (CH), 160.1 (C).

4-Ethoxy-N,N-dimethylaniline **2g**
Obtained in 90% yield as a wax. m.p.: 35–37°C (lit. (*33*) 35°C); δ_H (360.13 MHz, $CDCl_3$) 1.34 (t, 3H), 2.72 (s, 6H), 3.94 (q, 2H), 6.51 (d, 2H), 6.78 (d, 2H); δ_C (90.55 MHz, $CDCl_3$) 14.9 (CH_3), 30.6 ($2CH_3$), 63.4 (CH_2), 112.7 (2CH), 115.4 (2CH), 144.4 (C), 150.0 (C).

1-Tert-butyl-4-ethoxybenzene **2h**
Obtained in 89% yield as an oil. δ_H (360.13 MHz, $CDCl_3$) 1.46 (s, 9H), 1.55 (t, 3H), 4.19 (q, 2H), 7.03 (d, 2H), 7.47 (d, 2H); δ_C (90.55 MHz, $CDCl_3$) 14.8 (CH_3), 29.7 (C), 31.5 ($3CH_3$), 63.6 (CH_2), 114.1 (2CH), 126.2 (2CH), 143.4 (C), 156.4 (C).

Ethoxybenzene **2i**
Obtained in 71% yield as a liquid with b.p.: 72–78°C/4.0–4.6 kPa (lit. (*34*): 72–73°C/4.5 kPa). δ_H (360.13 MHz, $CDCl_3$) 1.41 (t, 3H), 4.07 (q, 2H),

7.02 (m, 3H), 7.35 (m, 2H); δ_C (90.55 MHz, $CDCl_3$) 14.4 (CH_3), 63.5 (CH_2), 114.4 (2CH), 120.3 (2CH), 129.2 (C), 158.6 (C).

4-Ethoxy-benzoic acid ethyl ester **2j**
Obtained in 93% yield as an oil. δ_H (360.13 MHz, $CDCl_3$) 1.26 (t, 3H), 1.33 (t, 3H), 3.95 (q, 2H), 4.27 (q, 2H), 6.80 (d, 2H), 7.92 (d, 2H); δ_C (90.55 MHz, $CDCl_3$) 14.0 (CH_3), 14.2 (CH_3), 60.1 (CH_2), 63.2 (CH_2), 113.6 (2CH), 122.3 (C), 131.1 (2CH), 162.3 (C), 165.9 (C).

2-Ethoxy-benzoic acid ethyl ester **2k**
Obtained in 92% yield as an oil. δ_H (360.13 MHz, $CDCl_3$) 1.29 (t, 3H), 1.291.37 (t, 3H), 4.02 (q, 2H), 4.29 (q, 2H), 6.88 (m, 2H), 7.35 (m, 1H), 7.69 (m, 1H); δ_C (90.55 MHz, $CDCl_3$) 13.9 (CH_3), 14.3 (CH_3), 60.3 (CH_2), 64.1 (CH_2), 112.9 (CH), 119.7 (CH), 120.5 (C), 131.0 (CH), 132.8 (CH), 158.0 (C), 166.2 (C).

Conclusion

Based on the performed experiments, we put forward a general, environmentally more acceptable method of ArOEt synthesis using DEC as the alkylating agent. Benign and useful by-products, such as ethanol, carbon dioxide, sodium sulfate and ferric hydroxide, are the only by-products produced in this reaction.

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