1-nitropropane, or 1-nitropentane), and sodium methylate were dissolved in the appropriate volume of methanol. The solution was refluxed for 2–3 h, cooled, and diluted with water. Extraction with ether and evaporation of the dried ether solution gave an oily residue which was triturated with methanol to give a white solid which was recrystallized from methanol. The present method is more convenient than the literature[10,11] methods for preparing nitro ketones **8a**,**d**.

4-Nitro-1,3-diphenyl-1-pentanone (8a). A solution of benzalacetophenone (4 g, 19 mmol), nitroethane (1.4 g, 18 mmol), and sodium methylate (1.02 g, 19 mmol) in methanol (50 mL) was used: yield 3.25 g (60%); mp 102–104 °C (lit.[11] mp 90–92 °C).

4-Nitro-1,3-diphenyl-1-hexanone (8b). A solution of benzalacetophenone (4 g, 19 mmol), 1-nitropropane (1.69 g, 19 mmol), and sodium methylate (1.02 g, 19 mmol) in methanol (50 mL) was used: yield 2.62 g (46%); mp 157–158 °C (lit.[12] mp 156–158 °C).

4-Nitro-1,3-diphenyl-1-octanone (8c). A solution of benzalacetophenone (10 g, 45 mmol), 1-nitropentane (5.62 g, 48 mmol), and sodium methylate (2.6 g, 48 mmol) in methanol (100 mL) was used: yield 8.59 g (55%); mp 70–71 °C; IR (KBr) 1683, 1545, 1450, 1370, 1240, 764, 750, 702, 688 cm^{-1}; NMR (CDCl$_3$) δ 0.98 (m, 9 H), 3.39 (m, 2 H), 3.94 (m, 1 H), 4.85 (m, 1 H), 7.65 (m, 10 H). Anal. Calcd for $C_{20}H_{23}NO_3$: C, 73.82; H, 7.12; N, 4.32. Found: C, 73.68; H, 7.06; N, 427.

6-Nitro-5-phenyl-2,2-dimethyl-3-heptanone (8d). A solution of 5-phenyl-2,2-dimethyl-4-penten-3-one (**6b**, 3 g, 20 mmol), nitroethane (1.5 g, 20 mmol), and sodium methylate (1.2 g, 20 mmol) in methanol (50 mL) was used: yield 1.35 g (30%); mp 57–59 °C (lit.[10] mp 61–62 °C).

General Procedure for the Preparation of Bromo Nitro Ketones[9] 9a–d. To a solution of the specific nitro ketone in chloroform was added bromine dropwise during refluxing. A drop of acetone was added to initiate the reaction. In cases where the red color of bromine disappeared, more bromine was added until a reddish color persisted. The extent of the reaction was periodically monitored by TLC and refluxing was stopped upon the disappearance of all or most of the starting material. The solvent was evaporated under reduced pressure and the yellow oily residue was triturated with methanol to yield a white solid which was recrystallized from methanol.

4-Nitro-1,3-diphenyl-2-bromo-1-pentanone (9a): 4-nitro-1,3-diphenyl-1-pentanone (**8a**, 2 g, 7 mmol) in chloroform (10 mL) and bromine; reflux time 15 min; yield 1.2 g (67%); mp 154–155 °C; IR (KBr) 1685, 1545, 1448, 1388, 1330, 1280, 805, 740, 680 cm^{-1}; NMR (CDCl$_3$) δ 1.38 (d, 3 H), 3.94 (d of d, 1 H), 5.07 (m, 1 H), 5.98 (d, 1 H), 7.47 (m, 8 H), 8.21 (m, 2 H). Anal. Calcd for $C_{17}H_{16}BrNO_3$: C, 56.37; H, 4.45; N, 3.86; Br, 22.06. Found: C, 56.38; H, 4.49; H, 3.83; Br, 22.27.

4-Nitro-1,3-diphenyl-2-bromo-1-hexanone (9b): 4-nitro-1,3-diphenyl-1-hexanone (**8b**, 1 g, 3.3 mmol) in chloroform (10 mL) and bromine; reflux time 15 min; yield 0.79 g (62%); mp 151–153 °C; IR (KBr) 1680, 1590, 1545, 1448, 1368, 1273, 1225, 740, 695, 682, 662 cm^{-1}; NMR (CDCl$_3$) δ 0.93 (t, 3 H), 1.72 (m, 2 H), 4.06 (d of d, 1 H), 4.84 (m, 1 H), 5.86 (d, 1 H), 7.31 (m, 8 H), 8.33 (m, 2 H). Anal. Calcd for $C_{18}H_{18}BrNO_3$: C, 57.46; H, 4.82; N, 3.72; Br, 21.24. Found: C, 57.46; H, 4.82; N, 3.74; Br, 21.4.

4-Nitro-1,3-diphenyl-2-bromo-1-octanone (9c): 4-nitro-1,3-diphenyl-1-octanone (**8c**, 2 g, 6 mmol) in chloroform (10 mL) and bromine reflux time 2 h; yield 0.74 g (30%); mp 137–138 °C; IR (KBr) 1682, 1550, 1450, 1365, 1277, 810, 700, 685 cm^{-1}; NMR (CDCl$_3$) δ 1.19 (m, 9 H), 3.91 (d of d, 1 H), 5.43 (m, 1 H), 6.06 (d, 1 H), 7.35 (m, 8 H), 7.93 (m, 2 H). Anal. Calcd for $C_{20}H_{22}BrNO_3$: C, 59.39; H, 5.53; N. 3.46; Br, 19.75. Found: C, 59.49; H, 5.46; N, 3.41; N, 3.41; Br, 19.3.

6-Nitro-5-phenyl-4-bromo-2,2-dimethyl-3-heptanone (9d): 6-nitro-5-phenyl-2,2-dimethyl-3-heptanone (**8d**, 0.5 g, 2.16 mmol) in chloroform (10 mL) and bromine; reflux time 2.5 h; yield 0.23 g (34%); mp 145–146 °C; IR (KBr) 2980, 1708, 1500, 1400, 1370, 1350, 1105, 1062, 761, 745, 708 cm^{-1}; NMR (CDCl$_3$) δ 0.99 (s, 9 H), 1.48 (d, 3 H), 3.70 (d of d, 1 H), 5.56 (m, 2 H), 7.42 (s, 5 H). Anal. Calcd for $C_{15}H_{20}BrNO_3$: C, 52.64; H, 5.89; N, 4.09; Br, 23.35. Found: C, 52.55; H, 5.90; N, 4.07; Br, 23.3.

General Procedure for the Preparation of Dihydrodipyrrol[1,2-*b*:3′,2′-*d*]isoxazole-3,4-dione 1-Oxides 11a–c. The specific bromo nitro ketone was treated with methanolic potassium hydroxide (0.5 N). The mixture was magnetically stirred for 30–60 min until all the solid was dissolved. The resulting solution was poured into iced hydrochloric acid and extracted with chloroform, the solvent was evaporated under reduced pressure, and the dark purple oily residue was triturated with ethanol to give a yellow solid which was recrystallized from toluene–ethanol (2:1).

(3a*R,3b*S**,8a*S**)-3a,8a-Dihydro-6,8a-dimethyl-2,3a,3b,5-tetraphenyl-3*H*-dipyrrol[1,2-*b*:3′,2′-*d*]isoxazole-3,4(3b*H*)-dione 1-Oxide (11a).** 4-Nitro-1,3-diphenyl-2-bromo-1-pentanone (**9a**, 1 g, 2.7 mmol) was treated with 5% methanolic potassium hydroxide solution (40 mL): yield 76 mg (10%); mp 195–196 °C; IR (KBr) 1720 (sh), 1710, 1610, 1540, 1490, 1450, 1405, 1387, 1373, 1320, 1200, 870, 690 cm^{-1}; NMR (CDCl$_3$) δ 1.08 (s, 3 H), 2.38 (s, 3 H), 7.37 (m, 16 H), 8.37 (m, 4 H). Anal. Calcd for $C_{34}H_{26}N_2O_4$: C, 77.55; H, 4.98; N, 5.32. Found: C, 77.55; H, 5.08; N, 5.29.

(3a*R,3b*S**,8a*S**)-6,8a-Diethyl-3a,8a-dihydro-2,3a,3b,5-tetraphenyl-3*H*-dipyrrol[1,2-*b*:3′,2′-*d*]isoxazole-3,4(3b*H*)-dione 1-Oxide (11b).** 4-Nitro-1,3-diphenyl-2-bromo-1-hexanone (**9b**, 0.5 g, 1.3 mmol) was treated with 5% methanolic potassium hydroxide (20 mL): yield 40 mg (10%); mp 193–194 sC; IR (KBr) 1720 (sh), 1710, 1610, 1532, 1490, 1450, 1400, 1320, 877, 749, 690 cm^{-1}; NMR (CDCl$_3$) δ 0.00 (t, 3 H), 1.28 (t, 3 H), 2.68 (m, 4 H), 7.36 (m, 16 H), 8.42 (m, 4 H); mass spectrum, m/e 554 (M$^+$, 100); 227 (M$^+$/2, 48). Anal. Calcd for $C_{36}H_{30}N_2O_4$: C, 77.96; H, 5.45; N, 5.05. Found: C, 77.59; H, 5.59; N, 5.01.

(3a*R,3b*S**,8a*S**)-6,8a-Dibutyl-3a,8a-dihydro-2,3a,3b,5-tetraphenyl-3*H*-dipyrrol[1,2-*b*:3′,2′-*d*]isoxazole-3,4(3b*H*)-dione 1-Oxide (11c).** 4-Nitro-1,3-diphenyl-2-bromo-1-octanone (**9c**, 0.5 g, 1 mmol) was treated with 5% methanolic potassium hydroxide (20 mL): yield 40 mg (10%); mp 159–160 °C; IR (KBr) 1725 (sh), 1710, 1630, 1532, 1450, 1395, 1370, 1320, 750, 693 cm^{-1}; NMR (CDCl$_3$) δ 1.5 (m, 18 H), 7.34 (m, 16 H), 8.44 (m, 4 H). Anal. Calcd for $C_{40}H_{38}N_2O_4$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.50; H, 6.30; N, 4.52.

Registry No. 6 (R^1 = t-Bu), 538-44-3; 6 (R^1 = Ph), 94-41-7; **8a**, 6277-76-5; **8b**, 80460-05-5; **8c**, 90552-85-5; **8d**, 90552-86-6; **9a**, 6289-91-4; **9b**, 90552-87-7; **9c**, 90552-88-8; **9d**, 90552-89-9; **10a**, 90552-90-2; **10b**, 90552-91-3; **10c**, 90552-92-4; **11a**, 90552-93-5; **11b**, 90552-94-6; **11c**, 90552-95-7; nitroethane, 79-24-3; 1-nitropropane, 108-03-2; 1-nitropentane, 628-05-7.

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A Convenient Synthesis of 12,12,12-Trifluorododecanoic Acid

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Reactions between anodically generated trifluoromethyl radicals and various olefins have been described several times,[1-5] but they have been little used for the practical synthesis of trifluoromethyl derivatives because of their somewhat low yields and because they often give mixtures containing about half a dozen products in which dimeric material or bis(trifluoromethyl) derivatives predominate. That the method deserves further exploration is suggested by the fact that electrolysis of trifluoroacetic acid (1) can

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provide 1 mol of trifluoromethyl radicals at roughly $^1/_{40}$ of the cost required to obtain them from iodotrifluoromethane,[6] while enough sulfur tetrafluoride to produce 1 mol of trifluoromethyl groups[7] costs at least 15 times as much as 1 mol of **1**. Thus even a 10–15% conversion of **1** to a readily isolated trifluoromethylated product may sometimes represent the most economical and perhaps also the least cumbersome procedure. This is illustrated by the work reported here, which shows that electrolysis of solutions of **1** and undecylenic acid (**2**) produces mixtures from which pure 12,12,12-trifluorododecanoic acid (**3**) can be easily prepared with a yield of 12.4% based on **1**.

Electrolysis of **1** in the presence of linear 1-alkenes was described in some detail in ref 4. When 0.1 or 0.2 mol of alkene dissolved in 40 mL of acetonitrile and 5.6 mL of water was used, the principal trifluoromethylated product was dimeric, but fractions containing the corresponding (trifluoromethyl)alkane, several isomeric 1-(trifluoromethyl)alkenes, and sometimes the 1,2-bis(trifluoromethyl)alkane were also obtained. The information given is not sufficient to allow the relative amounts of these products to be calculated, but they appear not to change greatly with the molecular weight of the alkene or the relative amounts of **1** and alkene taken. Attempts made here to effect larger changes in the product distribution by modifying the reaction conditions also met little success, though it seems that dimer formation could be somewhat reduced by using acetone/water and working at lower alkene concentrations. With **2**, as with the simple alkenes, pouring the reaction mixture into water gave an oil from which it was not readily possible to isolate a single component by distillation. However, it is a great advantage that now the desired ultimate product **3** is solid at room temperature. A preliminary distillation gave a fraction containing unreacted **2** and the mixed monomeric products, which was catalytically hydrogenated to convert **2** to undecanoic acid and the isomeric (trifluoromethyl)undecenoic acids to **3**. On distilling again, a fraction rich in **3** was collected from which the pure product was obtained by recrystallization from acetonitrile. The major impurity, undecanoic acid, is quite soluble in this solvent[8] even at 0 °C, while **3**, like dodecanoic acid,[8] is very soluble at room temperature but only sparingly soluble at 0 °C.

Compound **3** was previously prepared in this laboratory several times by the reaction of dodecanedioic acid with sulfur tetrafluoride.[9] The electrochemical synthesis is without question the easier one, especially when fairly large amounts of the product are needed. Other acids in the series $CH_2{=}CH(CH_2)_nCOOH$ should react analogously but are considerably more difficult to obtain.

Experimental Section

Commercial samples of the starting materials and solvent were used as received. Each reaction mixture consisted of 30 mL (389 mmol) of **1**, 60.6 mL (300 mmol) of **2**, 144 mL of acetone, and 36 mL of water. The customary step of partially neutralizing the solution with a little sodium hydroxide was omitted because this was found not to affect the course of the reaction significantly. The electrolysis cell was as described before.[5] Fluorine NMR spectra of aliquots withdrawn at various times indicated that the monomeric products reached optimal concentrations when about 0.48 Faraday had passed through the cell, which was achieved by using an approximately constant current of 0.54 A for 24 h. The mixture was then poured into 700 mL of water, the dense oil isolated, and the water layer extracted with 2 × 50 mL of methylene chloride. The combined nonaqueous layers from five identical runs were distilled at 1 atm to remove volatile solvents and then at about 1 torr, with all the material boiling below 140 °C (mostly 105–130 °C) being collected as a single fraction weighing 170 g. This was diluted with 100 mL of glacial acetic acid and hydrogenated at low pressure over 5% Pd/C catalyst until hydrogen absorption ceased and the NMR spectrum no longer showed signals characteristic of the unsaturated products. After removal of the catalyst the mixture was distilled again at 1 torr by using a short Vigreux column and an air-cooled condenser. The boiling point rose more or less steadily during this distillation, and the distillate was collected in four fractions weighing 45, 32, 75, and 6 g and corresponding to boiling ranges of 95–106 °C, 106–110 °C, 110–116 °C, and 116–124 °C, respectively. This first of these consisted mostly of undecanoic acid, while **3** was most concentrated in the large third fraction, which partially sodified during the distillation. This was dissolved in 300 mL of acetonitrile and stored in the refrigerator overnight, and 43.4 g of **3** slightly contaminated with undecanoic acid were isolated. The filtrate and washings were distilled to remove acetonitrile and then vacuum distilled with the smaller fractions to obtain more product-rich material, which on treatment with acetonitrile yielded a further 17.1 g of solid. Repetition of this procedure produced another 4.1 g. On further recrystallization from acetonitrile the combined solids gave 57.6 g of pure **3**. This material did not show the methyl triplet of undecanoic acid in its ^1H NMR spectrum, and its spectra and melting point agreed with those of **3** prepared by the sulfur tetrafluoride procedure.[9] A second crop of somewhat lower purity weighed 3.6 g, bringing the total yield to 12.4% based on **1** or 16.0% based on **2**. The yield can be slightly improved if the remaining product-containing residues are worked up with crude material from a subsequent preparation.

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Photochemical Reactions in Constrained Systems: Changes in Mode of Solubilization due to Long-Chain Hydrophobic Groups

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The usefulness of organized media to bring about regioselectivity in photocycloadditions by surfactant aggregates has been demonstrated.[1-5] In general, hydrophilic groups such as carbonyl or hydroxyl have been used to orient these molecules at the micelle–water interface. Recently we have shown that micellar-induced preorientations have limitations.[6] The dimerization of 7-alkoxycoumarins in SDS and CTAB micelles was expected to lead to syn and/or anti head–head dimer by virtue of the aggregation of coumarin molecules at the interface in which carbonyl groups would face the aqueous exterior while the anchoring alkoxy groups held the coumarin solubilizates in an ordered row. Such an expectation however was not borne out. Since chain lengths up to C_{12} failed to bring

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