Novel liquid crystal compounds, derivatives of 2-pyrone

L. I. Zakharkin, S. V. Sokolovskaya, L. K. Moldovanova, and V. V. Guseva*

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095) 135 5085

6-(4-*n*-Hexyloxyphenyl)- and 6-(4-*n*-decyloxyphenyl)-2-pyrones, which possess smectic and nematic mesomorphism, were synthesized.

Key words: acetophenone alkoxy-derivatives, 5-(alkoxyphenyl)-1,1-dichloropenta-1,3-dien-2-ones, 6-(4-*n*-alkoxyphenyl)-2-pyrones, 6-(4-*n*-alkoxyphenyl)-3-iodo-2-pyrones.

The introduction of heterocycles to molecules of liquid crystal compounds affects their transition temperatures, the type of the mesophase, and the sign and structure of dielectric anisotropy.[1] Previously,[2] liquid crystal compounds, namely, derivatives of 1,3-dioxane, possessing smectic and nematic mesomorphism have been obtained. In a continuation of the study of 6-aryl-2-pyrones[3–5] we synthesized 6-(4-alkoxyphenyl)-2-pyrones. Among these compounds, we found novel liquid crystal compounds, whose molecules incorporate an oxygen-containing heterocycle.

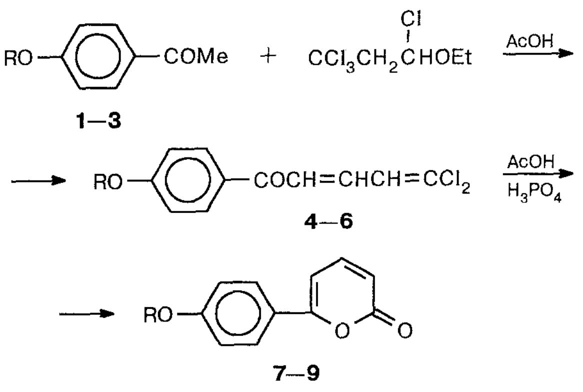
Condensation of 4-alkoxyacetophenones **1**—**3** with 1,1,1,3-tetrachloro-3-ethoxypropane in AcOH according to the procedure described previously[6] gave dichlorodienic ketones **4**—**6** in high yields. The latter compounds were heated in AcOH in the presence of a catalytic amount of H_3PO_4 to afford 6-(4-alkoxyphenyl)-2-pyrones **7**—**9** (Scheme 1).

Pyrones **7** and **8**, unlike pyrone **9**, are compounds with liquid crystal properties. Compound **7** displays the properties of smectic and nematic liquid crystals, with phase transition temperatures 28 °C (K→S), 45 °C (S→N), and 120 °C (N→I), while compound **8** has the properties of nematic liquid crystals with the corresponding temperatures of 85 °C (K→N) and 120 °C (N→I), where S indicates the smectic state, N is the nematic state, and I is an isotropic liquid.

The reaction of pyrones **7** and **9** with iodine in the presence of phenyliodoso trifluoroacetate according to the known procedure[7] gave 3-iodopyrones **10** and **11** (Scheme 2). The reaction of iodopyrone **11** with CuCN occurs smoothly *via* replacement of the I atom by a CN group to give cyanopyrrone **12**.

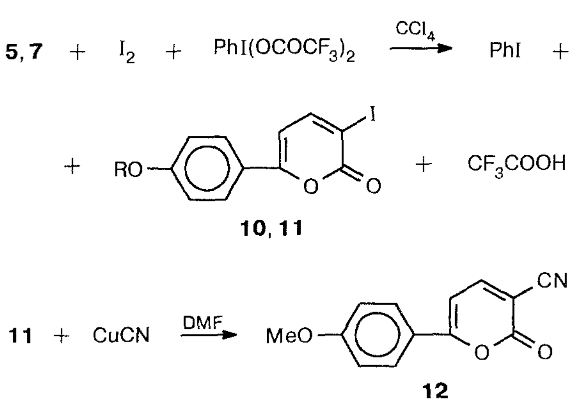
Compounds **10** and **12** do not display liquid crystal properties. Thus, substituted 6-aryl-2-pyrones display liquid crystal properties only if they contain an alkoxy group with at least six C atoms at the *para* position of the benzene ring.

Scheme 1



1,4,7: R = $C_6H_{13}^n$
2,5,8: R = $C_{10}H_{21}^n$
3,6,9: R = Me

Scheme 2



10: R = $C_6H_{13}^n$
11: R = Me

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1793—1794, October, 1994.

Experimental

1,1,1,3-Tetrachloro-3-ethoxypropane was obtained by the procedure reported in Ref. 8.

4-(*n*-Hexyloxy)acetophenone (1). A mixture of 4-hydroxyacetophenone (13.6 g, 0.1 mol), hexyl bromide (18.56 g, 0.113 mol), K_2CO_3 (14.5 g, 0.105 mol), KI (1.66 g, 0.01 mol), and EtOH (20 mL) was refluxed for 40 h. The residue was filtered off and the mother liquor was diluted with water. The resulting oil was extracted with ether, and the ethereal solution was washed with water and dried with Na_2SO_4. Removal of the ether by distillation gave 19.4 g (88 %) of compound **1**, b.p. 148—149 °C (2 Torr), n_D^{20} 1.5151.

4-(*n*-Decyloxy)acetophenone (2) was obtained similarly to compound **1** (reaction time 35 h). The yield of ketone **2** was 68 %, m.p. 36—38 °C (hexane). Found (%): C, 78.16; H, 9.73. $C_{18}H_{28}O_2$. Calculated (%): C, 78.26; H, 10.15.

1,1-Dichloro-5-(4-*n*-hexyloxyphenyl)penta-1,3-dien-1-one (4). A solution of compound **1** (6.6 g, 0.03 mol) and 1,1,1,3-tetrachloro-3-ethoxypropane (8.4 g, 0.037 mol) in AcOH (10 mL) was kept for 4 days at 20 °C and poured into water. The mixture was extracted with ether. The ethereal extracts were washed with a solution of $NaHCO_3$ and water and dried with $MgSO_4$. The solvent was removed and the residue was chromatographed on SiO_2 using benzene as the eluent to give 7.5 g (76.5 %) of dichloroketone **4**, m.p. 54—55 °C (from ethanol). Found (%): C, 62.24; H, 6.21; Cl, 21.53. $C_{17}H_{20}Cl_2O_2$. Calculated (%): C, 62.38; H, 6.12; Cl, 21.72.

1,1-Dichloro-5-(4-*n*-decyloxyphenyl)penta-1,3-dien-1-one (5). A mixture of compound **2** (5.5 g, 0.02 mol), 1,1,1,3-tetrachloro-3-ethoxypropane (3 g, 0.013 mol), and glacial AcOH (15 mL) was stirred for 3 days at 20 °C. The resulting precipitate was filtered off to give 5.5 g (72 %) of dichloroketone **5** as light-yellow crystals, m.p. 69—70 °C (from ethanol). Found (%): C, 65.85; H, 7.35; Cl, 18.45. $C_{21}H_{28}Cl_2O_2$. Calculated (%): C, 65.80; H, 7.31; Cl, 18.54.

1,1-Dichloro-5-(4-methoxyphenyl)penta-1,3-dien-1-one (6). A mixture of 4-methoxyacetophenone (3.8 g, 0.025 mol), 1,1,1,3-tetrachloro-3-ethoxypropane (6.8 g, 0.0294 mol), and 98 % AcOH (35 mL) was kept for 5 days at 20 °C. The crystals that precipitated were filtered off and washed with MeOH (5 mL) to give 3.66 g (53.5 %) of dichloroketone **6** as greenish crystals, m.p. 116.5—117.5 °C (*cf.* Ref. 9: m.p. 117—118 °C).

6-(4-*n*-Hexyloxyphenyl)-2-pyrone (7). A mixture of dichloroketone **4** (2 g, 0.0061 mol) in AcOH (15 mL) and H_3PO_4 (0.2 mL) was boiled for 23 h until HCl ceased evolving, cooled to ~20 °C, and poured into water. The crystals that precipitated were repeatedly washed with water and dried to give 7.3 g (73 %) of pyrone **7** as yellow crystals, m.p. 28—45—120 °C (pentane). Found (%): C, 74.57; H, 7.25. $C_{17}H_{20}O_3$. Calculated (%): C, 75.00; H, 7.35.

6-(4-*n*-Decyloxyphenyl)-2-pyrone (8) was obtained similarly to pyrone **7** from dichloroketone **5** (5.3 g, 0.0138 mol), yield 4 g (88.5 %) of pyrone **8**, m.p. 85—120 °C (pentane). Found (%): C, 76.70; H, 8.43. $C_{21}H_{28}O_3$. Calculated (%): C, 76.83; H, 8.54.

6-(4-Methoxyphenyl)-2-pyrone (9) was obtained similarly to pyrone **7** from dichloroketone **6**, yield 6.02 g (96 %) of pyrone **9**, m.p. 96.5—97.5 °C (benzene—heptane) (*cf.* Ref. 9: m.p. 96—97 °C).

6-(4-*n*-Hexyloxyphenyl)-3-iodo-2-pyrone (10). A solution of pyrone **7** (2.72 g, 0.01 mol), I_2 (1.5 g, 0.006 mol), and $PhI(OCOCF_3)_2$ (4.02 g, 0.009 mol) in CCl_4 (50 mL) was stirred for 2 days at 20 °C. The reaction mixture was worked-up with a $Na_2S_2O_3$ solution, and the organic layer was washed with water and dried with $MgSO_4$. The solvent was removed to leave 1.6 g (40 %) of iodopyrone **10**, m.p. 135—137 °C (EtOH). Found (%): C, 50.92; H, 4.88; I, 30.81. $C_{17}H_{19}IO_3$. Calculated (%): C, 51.26; H, 4.77; I, 30.91.

3-Iodo-6-(4-methoxyphenyl)-2-pyrone (11). A solution of pyrone **7** (2 g, 0.01 mol), I_2 (1.56 g, 0.0061 mol), and $PhI(OCOCF_3)_2$ (4.02 g, 0.009 mol) in CCl_4 (10 mL) was stirred for 2 days at 20 °C. The resulting crystals were filtered off to give 1.97 g (60 %) of compound **11**, m.p. 161—162 °C (EtOH). Found (%): C, 43.51; H, 2.69; I, 39.27. $C_{12}H_9IO_3$. Calculated (%): C, 44.00; H, 2.75; I, 39.00.

3-Cyano-6-(4-methoxyphenyl)-2-pyrone (12). Compound **11** (1 g, 0.003 mol) and CuCN (0.5 g, 0.0056 mol) were refluxed for 6 h in dry DMF (10 mL). The mixture was poured into water and extracted with chloroform; the organic layer was washed with water and dried with $MgSO_4$. The solvent was distilled off, and the solid precipitate was crystallized from ethanol to give 0.5 g (71 %) of cyanopyrone **12** as yellow crystals, m.p. 179—180 °C. Found (%): C, 68.52; H, 3.81; N, 5.84. $C_{13}H_9NO_3$. Calculated (%): C, 68.73; H, 3.96; N, 6.17.

References

1. M. M. Murza, M. G. Safarov, and R. M. Nazmukhanova, *Zh. Org. Khim.*, 1984, **20**, 132 [*J. Org. Chem. USSR*, 1984, **20** (Engl. Transl.)].
2. M. M. Murza and M. G. Safarov, *Zh. Org. Khim.*, 1993, **29**, 193[*J. Org. Chem. USSR*, 1993, **29** (Engl. Transl.)].
3. L. I. Zakharkin and L. P. Sorokina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1958, 1445 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1958, No. 12 (Engl. Transl.)].
4. Yu. V. Maevskii and S. V. Sokolovskaya, *Khim. Geterotsikl. Soedin.*, 1971, 579 [*Chem. Heterocycl. Compd.*, 1971 (Engl. Transl.)].
5. S. V. Sokolovskaya and L. K. Moldovanova, *Khim. Geterotsikl. Soedin.*, 1976, 998 [*Chem. Heterocycl. Compd.*, 1976 (Engl. Transl.)].
6. L. P. Sorokina and L. I. Zakharkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1964, 73 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1964, **13**, No. 1 (Engl. Transl.)].
7. S. V. Sokolovskaya and L. K. Moldovanova, *Izv. Vuz. Khim. Khim. Tekhnol.* [*Bull. High. Inst. Chem. Technol.*], 1987, **30**, 106 (in Russian).
8. A. N. Nesmeyanov, R. Kh. Freidlina, and L. I. Zakharkin, *Dokl. Akad. Nauk SSSR*, 1954, **97**, 91 [*Dokl. Chem.*, 1954, **97** (Engl. Transl.)].
9. M. Julia and J. Bullot, *Bull. Soc. Chim. France*, 1960, 23.

Received April 29, 1994