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CHROMATOGRAPHY OF MONOMERS

VI. NEW DERIVATIVE FOR IMPROVED THIN-LAYER CHROMATOGRAPHIC SEPARATION OF C_1–C_{18} ALKYL ESTERS OF ACRYLIC ACID

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SUMMARY

The utility of the reaction between alkyl acrylates and diazomethane was investigated. The whole homologous series of C_1–C_{18} *n*-alkyl-3-alkoxycarbonyl-2-pyrazolines migrate with binary systems containing benzene and ethyl acetate on Silufol. Cellulose and octadecyl-bonded silica gel were also used as sorbents. The migration order of derivatives observed on paraffin oil impregnated Silufol is not consistent with that on dimethylformamide impregnated Celufol or Lucefol.

INTRODUCTION

We have previously published[1,2] methods for thin-layer chromatographic (TLC) separation of C_2–C_{18} alkyl esters of acrylic and methacrylic acids. The poor separation of some neighbouring members in each homologous series led us to seek suitable derivatives.

The reaction of diazomethane with α-unsaturated carbonyl compounds to form pyrazolines is well known[3]. It was found that ethyl acrylate reacts rapidly with diazomethane in diethyl ether to give 3-alkoxycarbonyl-1-pyrazoline[4,5]. The latter readily tautomerizes in the presence of alcohols to the more stable 2-pyrazoline[4]. The pyrazolines give strongly yellow derivatives with Ehrlich reagent, and with 4-dimethylaminocinnamaldehyde even more intense and more stable purple derivatives were formed[6].

As a continuation of our chromatographic studies[1,2,7–9] dealing with acrylic and methacrylic monomers, this paper describes the TLC behaviour of 3-alkoxycarbonyl-2-pyrazolines, prepared from C_1–C_{18} *n*-alkyl acrylates by diazomethane addition, on silica gel, cellulose and octadecyl-bonded silica high-performance plates with various developing systems.

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EXPERIMENTAL

Reagents

The acrylates were either of commercial origin or prepared by the sulphuric acid-catalysed esterification of acrylic acid and commercial aliphatic alcohols. 4-Dimethylaminocinnamaldehyde was prepared in our laboratory by a modified method[10], involving the reaction of 4-dimethylaminobenzaldehyde with acetaldehyde in the presence of concentrated sulphuric acid at 0°C (cooling with ice water).

The other chemicals including solvents were obtained from Lachema (Brno, Czechoslovakia) or Chemapol (Praha, Czechoslovakia). Analytical-reagent grade chemicals were used without further purification.

Diazomethane preparation

Diazomethane was prepared by the decomposition of N-methyl-N-nitroso-*p*-toluenesulphonamide with potassium hydroxide. The apparatus consisted of a three-neck flask connected to three impingers containing cooled diethyl ether. A stream of nitrogen was used to carry the diazomethane produced into the impingers. Because of the high toxicity and carcinogenity of diazomethane, all operations involving it were conducted in a well ventilated fume cupboard. The final concentration of the diazomethane solution was determined by titration.

Sample preparation

The stock solutions of the individual acrylates were prepared by dissolving 200 mg of the ester in 2 ml of methanol containing 0.1% (w/v) of tris(hydroxymethyl)-aminomethane (Tris)[6]. Then a calculated excess of diazomethane in diethyl ether solution was added. The reaction was carried out at room temperature. The final products were analysed by elemental analysis, gas chromatography–chemical ionization mass spectrometry (GC–MS) and high-performance liquid chromatography (HPLC).

Thin-layer chromatography

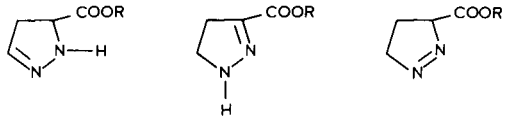
Silufol silica gel ready-made plates (20 cm × 20 cm), Lucefol and/or Celufol cellulose plates (15 cm × 15 cm) were obtained from Kavalier (Votice, Czechoslovakia). HPTLC plates RP-18 F_{254} S (10 cm × 10 cm) were obtained from Merck (Darmstadt, F.R.G.). In adsorption chromatographic mode, these materials, as usual, were utilized without further treatment. In reversed-phase liquid–liquid chromatography (LLC), the Silufol plates were impregnated with a 5% (v/v) solution of paraffin oil in light petroleum (b.p. 50–75°C). For normal-phase LLC, the Celufol and/or Lucefol plates were impregnated with 40% (v/v) dimethylformamide in ethanol.

Volumes from 1 to 2 μl, containing 1 μg of sample in 1 μl of methanol, were applied. After development, the thin-layer plates were left until dry. The spots were detected by spraying with diluted Ehrlich reagent or with an acidic solution of 4-dimethylaminocinnamaldehyde in ethanol. With the latter, purple spots appeared within a few minutes against a white ground. With Ehrlich reagent yellow spots against a white ground appeared.

RESULTS AND DISCUSSION

The products of the reaction between alkyl acrylates and diazomethane, *viz.* 3-alkoxycarbonyl-2-pyrazolines (II), were investigated by TLC. Freshly prepared samples gave only one spot on the chromatogram, when the appropriate amount of Tris solution was taken had been used in their preparation. However, 3 months later, HPLC showed more than one peak. Also, fused-silica capillary GC–MS analyses showed a main peak being accompanied by minor peaks due to isomers.

The complexity of the product may explain why pyrazolines derived from alkyl acrylates are rather unstable, there being three possible tautomeric forms, of which the 3-alkoxycarbonyl-2-pyrazoline (II) is the most stable[4]:



(I) (II) (III) R = alkyl chain

In spite of the presence of such tautomeric forms or of minor side products, diazomethylation is a promising method of derivatization of acrylates for their TLC separation and identification.

The TLC behaviour of 3-alkoxycarbonyl-2-pyrazolines (DA1–DA18) prepared from C_1–C_{18} *n*-alkyl esters of acrylic acid was studied on cellulose, silica gel and octadecyl-bonded silica thin layers with different developing solvents. The R_F values are summarized in Table I. The absence of a value in a particular solvent system indicates that the spot was located either at the start or so near to the front that its R_F could not accurately be determined.

Adsorption chromatography

None of the 3-alkoxycarbonyl-2-pyrazolines migrates in a single-component solvent such as hexane, tetrachloromethane, benzene or toluene. When polar solvents, *i.e.*, acetone or ethanol, were employed the derivatives moved migrated with the solvent front. The 3-alkoxycarbonyl-2-pyrazolines possess one acidic hydrogen and one basic nitrogen, so it is reasonable that these compounds show a large affinity towards polar adsorbents and solvents. Thus the compounds DA1–DA18 had moderate mobilities in low-polarity solvents such as hexane, cyclohexane or benzene containing a more polar modifier such as ethyl acetate, methyl ethyl ketone or acetone. Satisfactory separation of the whole homologous series of C_1–C_{18} *n*-alkyl 3-alkoxycarbonyl-2-pyrazolines was obtained with binary solvent systems containing benzene and ethyl acetate in the concentration (v/v) range of 7:3 (S_1) to 8:2 (S_2). However, the resolution of neighbouring spots in the middle of the homologous series was not complete. Reasonable separations of C_1–C_8 *n*-alkyl 3-alkoxycarbonyl-2-pyrazolines were obtained with the following simple mixtures of organic solvents: hexane–methyl ethyl ketone (7:3, v/v) (S_3); cyclohexane–ethyl acetate (6:4, v/v) (S_4); hexane–benzene–acetone (3:1:1, v/v) (S_5) and hexane–acetone (2:1, v/v) (S_6).

TABLE I

R_F VALUES OF 3-ALKOXYCARBONYL-2-PYRAZOLINES (DA1–DA18) PREPARED FROM C_1–C_{18} *n*-ALKYL ESTERS OF ACRYLIC ACID

S_1 = Silufol/benzene–ethyl acetate (7:3, v/v); S_2 = Silufol/benzene–ethyl acetate (8:2, v/v); S_3 = Silufol/hexane–methyl ethyl ketone (7:3, v/v); S_4 = Silufol/cyclohexane–ethyl acetate (6:4, v/v); S_5 = Silufol/hexane–benzene–acetone (3:1:1, v/v); S_6 = Silufol/hexane–acetone (2:1, v/v); S_7 = Silufol/5% paraffin oil/dimethylformamide–water–methanol (2:1:1, v/v); S_8 = Silufol/5% paraffin oil/dimethylformamide–water–methanol (2:2:1, v/v); S_9 = Celufol/40% dimethylformamide/cyclohexane–benzene (24:1, v/v); S_{10} = Celufol/40% dimethylformamide/paraffin oil–light petroleum ether (1:1, v/v); S_{11} = Celufol/40% dimethylformamide/light petroleum; S_{12} = HPTLC RP-18 $F_{254}S$/acetonitrile–water (3:1, v/v); S_{13} = HPTLC RP-18 $F_{254}S$/ methanol–water (3:1, v/v); S_{14} = Lucefol/40% dimethylformamide/cyclohexane–hexane (24:1, v/v).

Compound	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}	S_{11}	S_{12}	S_{13}	S_{14}
DA1	0.19	0.13	0.25	0.14	0.30	0.34	0.89	0.81	0.04	–	0.03	0.75	0.69	0.04
DA2	0.25	0.17	0.30	0.22	0.36	0.41	0.86	0.80	0.08	–	0.08	0.72	0.62	0.12
DA3	0.32	0.21	0.38	0.30	0.44	0.44	0.84	0.73	0.14	–	0.16	0.63	0.50	0.15
DA4	0.38	0.26	0.39	0.36	0.50	0.46	0.81	0.66	0.24	–	0.32	0.57	0.37	0.26
DA5	0.42	0.30	0.48	0.41	0.54	0.52	0.76	0.53	0.33	–	0.47	0.47	0.28	0.34
DA6	0.47	0.33	0.56	0.45	0.60	0.58	0.70	0.39	0.44	–	0.62	0.36	0.22	0.46
DA7	0.52	0.36	0.63	0.47	0.62	0.60	0.60	0.26	0.61	0.21	0.73	0.25	0.15	0.66
DA8	0.56	0.39	0.68	0.49	0.63	0.63	0.54	0.19	0.83	0.34	0.89	0.14	0.14	0.91
DA9	0.56	0.42					0.40	0.10	–	0.43	–	0.12	0.08	–
DA10	0.59	0.44					0.30	0.06	–	0.54	–	0.07	0.05	–
DA12	0.62	0.47					0.15	–	–	0.66	–	0.05	0.03	–
DA14	0.63	0.50					0.06	–	–	0.77	–	–	–	–
DA16	0.65	0.54					0.03	–	–	0.83	–	–	–	–
DA18	0.70	0.56					–	–	–	0.86	–	–	–	–

Liquid–liquid chromatography

For reversed-phase liquid chromatography we used Silufol impregnated with 5% paraffin oil, and aqueous solutions containing an organic modifier such as methanol or dimethylformamide as the mobile phases. Complete separation of the whole homologous series of C_1–C_{18} *n*-alkyl 3-alkoxycarbonyl-2-pyrazolines was accomplished with ternary mixtures of dimethylformamide–water–methanol (2:1:1, v/v/v) (S_7) or (2:2:1, v/v/v) (S_8). On octadecyl-bonded silica gel HPTLC plates, clear-cut separations of C_1–C_{14} *n*-alkyl derivatives was easily obtained with the use of acetonitrile–water (3:1, v/v) (S_{12}) and methanol–water (3:1, v/v) (S_{13}). On cellulose plates, Celufol impregnated with 40% solution dimethylformamide in ethanol, a relatively good separation of the studied derivatives was obtained. For resolution of C_1–C_8 *n*-alkyl homologues, the solvents cyclohexane–benzene (24:1, v/v) (S_9) and light petroleum (S_{11}) were most convenient. For resolution of higher C_7–C_{18} *n*-alkyl derivatives on 40% dimethylformamide impregnated Celufol, 50% (v/v) paraffin oil solution in light petroleum (S_{10}) was the most suitable solvent.

For the separation of C_1–C_8 *n*-alkyl 3-alkoxycarbonyl-2-pyrazolines, Celufol may be replaced by Lucefol. On 40% dimethylformamide-impregnated Lucefol, a very good separation of C_1–C_8 *n*-alkyl homologues was obtained with the binary mixture cyclohexane–hexane (24:1, v/v) (S_{14}).

It should be noted that the order of elution of the 3-alkoxycarbonyl-2-pyrazolines on paraffin oil-impregnated Silufol is not consistent with those on dimethylformamide-impregnated Celufol and/or Lucefol.

CONCLUSIONS

The improved separations of C_1–C_{18} *n*-alkyl 3-alkoxycarbonyl-2-pyrazolines in various TLC systems indicate that diazomethylation may be considered as a promising method of derivatization for acrylate monomer analyses.

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