

CHROM. 13,683

Note

Separation of isomeric thiohydantoins by thin-layer chromatography

G. N. MAHAPATRA* and H. P. DAS

Department of Chemistry, Ravenshaw College, Utkal University, Cuttack 753003 (India)

(Received January 29th, 1981)

During the synthesis of 2-thiohydantoins^{1,2}, 5,5-diaryl-, 3-aryl- and 5,5-diaryl-1,3-diaryl-2-thiohydantoins were obtained from benzils and various monoaryl- and sym.-diarylthioureas, respectively, and it was necessary to study the separation and identification of the final product by thin-layer chromatography (TLC). In recent years, this technique has also been applied successfully to the separation of isomeric compounds using suitable solvent systems³⁻⁶. The present investigation has shown that it is not only possible to separate thiohydantoins from corresponding thioureas but also to separate isomeric thiohydantoins from one another.

EXPERIMENTAL

A slurry was prepared by mixing 25 g of silica gel G (according to Stahl, Type 60; E. Merck, Darmstadt, G.F.R.) in 50 ml of distilled water. Ten well cleaned glass plates (20 × 10 cm) were coated with the adsorbent to a thickness of 250 μm using an adjustable Desaga Model S II (Stahl-type) applicator. When the layer had almost dried, the coated glass plates were activated by heating them in an air oven at 175°C for 45 min. The spotted plates were developed in air-tight glass chambers (25 × 12 × 25 cm) that had been previously saturated with the solvent vapour; the developing time was 58–80 min, depending on the solvent used. The operating temperature was 25–30°C and the relative humidity of the atmosphere was 60–70%. The developed chromatograms, after being dried, were sprayed with sodium azide and iodine-potassium iodide reagent followed by starch solution. The thiohydantoin compounds were detected as colourless spots on a bluish background.

RESULTS

A large number of solvent systems were tried, and those which gave reasonable differences in the R_f values of the isomers are listed in Table I. The separation of the isomeric compounds 5,5-di(*p*-chlorophenyl)-3-*o*-, *m*-, *p*-chlorophenyl-, 5,5-di(*p*-chlorophenyl)-1,3-di-*o*-, *m*-, *p*-chlorophenyl-2-thiohydantoins, 5,5-di(*p*-methoxyphenyl)-3-*o*-, *m*-, *p*-tolyl-, 5,5-di(*p*-methoxyphenyl)-1,3-di-*o*-, *m*-, *p*-tolyl-2-thiohydantoins and 5,5-distyryl-3-*o*-, *m*-, *p*-nitrophenyl-, 5,5-distyryl-1,3-di-*o*-, *m*-, *p*-nitrophenyl-2-thiohydantoins were studied.

An equimolar mixture of the isomeric compounds was chromatographed by

TABLE I

 R_F VALUES OF ISOMERS IN DIFFERENT SOLVENT SYSTEMS

Solvent systems: 1:1 mixtures of light petroleum (b.p. 60–80°C) with (A) benzene, (B) methanol, (C) ethanol, (D) isopropanol and (E) *n*-butanol.

Compound	R_F value				
	A	B	C	D	E
5,5-Di(<i>p</i> -chlorophenyl)-3- <i>o</i> -chlorophenyl-2-thiohydantoin	0.03	0.52	0.58	0.54	0.55
5,5-Di(<i>p</i> -chlorophenyl)-3- <i>m</i> -chlorophenyl-2-thiohydantoin	0.15	0.62	0.67	0.63	0.66
5,5-Di(<i>p</i> -chlorophenyl)-3- <i>p</i> -chlorophenyl-2-thiohydantoin	0.31	0.83	0.85	0.82	0.84
5,5-Di(<i>p</i> -chlorophenyl)-1,3-di- <i>o</i> -chlorophenyl-2-thiohydantoin	0.08	0.58	0.59	0.54	0.53
5,5-Di(<i>p</i> -chlorophenyl)-1,3-di- <i>m</i> -chlorophenyl-2-thiohydantoin	0.21	0.67	0.68	0.62	0.61
5,5-Di(<i>p</i> -chlorophenyl)-1,3-di- <i>p</i> -chlorophenyl-2-thiohydantoin	0.39	0.78	0.77	0.74	0.73
5,5-Di(<i>p</i> -methoxyphenyl)-3- <i>o</i> -tolyl-2-thiohydantoin	0.24	0.56	0.58	0.54	0.52
5,5-Di(<i>p</i> -methoxyphenyl)-3- <i>m</i> -tolyl-2-thiohydantoin	0.36	0.64	0.60	0.62	0.61
5,5-Di(<i>p</i> -methoxyphenyl)-3- <i>p</i> -tolyl-2-thiohydantoin	0.46	0.74	0.70	0.70	0.72
5,5-Di(<i>p</i> -methoxyphenyl)-1,3-di- <i>o</i> -tolyl-2-thiohydantoin	0.34	0.32	0.31	0.30	0.83
5,5-Di(<i>p</i> -methoxyphenyl)-1,3-di- <i>m</i> -tolyl-2-thiohydantoin	0.39	0.44	0.43	0.42	0.47
5,5-Di(<i>p</i> -methoxyphenyl)-1,3-di- <i>p</i> -tolyl-2-thiohydantoin	0.49	0.51	0.52	0.51	0.56
5,5-Distyryl-3- <i>o</i> -nitrophenyl-2-thiohydantoin	0.41	0.45	0.43	0.42	0.41
5,5-Distyryl-3- <i>m</i> -nitrophenyl-2-thiohydantoin	0.58	0.57	0.56	0.53	0.51
5,5-Distyryl-3- <i>p</i> -nitrophenyl-2-thiohydantoin	0.67	0.64	0.62	0.61	0.60
5,5-Distyryl-1,3-di- <i>o</i> -nitrophenyl-2-thiohydantoin	0.40	0.41	0.40	0.41	0.39
5,5-Distyryl-1,3-di- <i>m</i> -nitrophenyl-2-thiohydantoin	0.51	0.56	0.54	0.54	0.52
5,5-Distyryl-1,3-di- <i>p</i> -nitrophenyl-2-thiohydantoin	0.62	0.62	0.61	0.62	0.61
Time of development (min)	58	62	80	75	65

ascending one-dimensional TLC. Effective separations of all of the above compounds were possible with 1:1 binary solvent systems of light petroleum (b.p. 60–80°C) with benzene, methanol, ethanol, isopropanol and *n*-butanol, marked differences in the R_F values of the *o*-, *m*- and *p*-isomers being obtained.

ACKNOWLEDGEMENTS

The authors are grateful to the U.G.C., Government of India, New Delhi, and the Board of Scientific and Industrial Research, Government of Orissa, India, for research grants in order to carry out this investigation.

REFERENCES

- 1 B. Behura, G. Panda, A. C. Rath and G. N. Mahapatra, *Indian J. Chem.*, 12 (1974) 781.
- 2 H. P. Das and G. N. Mahapatra, *Indian J. Chem.*, 18B (1979) 257.
- 3 Z. Czerwiec, *Chem. Anal. (Warsaw)*, 21 (1976) 751.
- 4 G. N. Mahapatra, H. Tripathy and G. Guru, *J. Chromatogr.*, 59 (1971) 461.
- 5 G. N. Mahapatra and H. Tripathy, *J. Chromatogr.*, 76 (1973) 493.
- 6 G. N. Mahapatra, J. P. Nath, B. K. Pattnaik and D. N. Rout, *J. Chromatogr.*, 193 (1980) 338.