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Note

Chromatography of organic compounds

III*. Improved procedure for the thin-layer chromatography of olefins on silver ion–silica gel layers**

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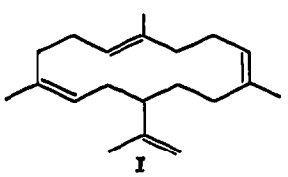
Thin-layer chromatography on silver nitrate–silica gel layers, first introduced[1–3] in the early 1960s, has now become an accepted technique for the separation of olefins (see, *e.g.*, ref. 4). However, no significant modification of the original technique has been introduced and the original procedures involving the use of layers of silica gel containing silver nitrate and gypsum continue to be employed. We have now found that silver perchlorate is superior to silver nitrate for certain olefin separations and that the presence of gypsum in these layers greatly diminishes the resolution.

During our work on the diterpene hydrocarbons of the gum-resin *Commiphora mukul* (Hook, *ex* Stocks)[5], we found that whereas it was difficult to prepare a silver nitrate complex of cembrene A (I), a silver perchlorate complex could easily be obtained. This suggested that a study of silver perchlorate in silica gel layers would be useful in order to find if this procedure will have any definite advantage over the use of silver nitrate–silica gel laminae. During this study it was observed that layers without a binder have good mechanical properties and afford better resolution. The present communication summarises these results.



I

EXPERIMENTAL

Materials

The silica gel used for this work was "Silica gel less than 0.08 mm for chromatography" (E. Merck, Darmstadt, G.F.R.). Sieve analysis showed that 97% passed through 200 mesh.

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Silver nitrate (laboratory reagent) was obtained commercially from Sarabhai Chemicals, Baroda, India.

Silver perchlorate, prepared according to a known procedure[6], was found to be acidic and catalyzed rearrangements of certain terpenes. Acid-free silver perchlorate was prepared as follows. Silver oxide was precipitated by the addition of 140 ml of 10% sodium hydroxide solution to silver nitrate solution (50.0 g in 250 ml of water) and the precipitate collected by filtration and thoroughly washed with water. This moist silver oxide was added in portions to aqueous perchloric acid (40 ml of 60% aqueous perchloric acid, further diluted with 50 ml of water) until the solution was neutral to litmus; further silver oxide was added and, after allowing the mixture to stand for 3 h at room temperature, it was filtered. The filtrate was freed from water by distillation from an oil-bath (125°) and the white residue (52 g) was stored in a dark bottle away from light. During all the above operations, exposure to direct light was avoided.

Plaster of Paris (—200 mesh) was a commercial sample.

Ethyl acetate (laboratory reagent) was used after distillation. Benzene was made thiophene-free, dried and distilled. Light petroleum, b.p. 60–64°, was freed from olefins by treating it with 1:1 concentrated sulphuric acid–concentrated nitric acid in the usual manner, commonly used for the purification of cyclohexane[7].

Terpene hydrocarbons (sesquiterpenes and diterpenes) were authentic samples available in this laboratory.

Preparation of plates

Silver nitrate or silver perchlorate (15 g) was dissolved in water (23 ml) and the solution slowly diluted with acetone (250 ml) with stirring, avoiding light. To the mixture, silica gel (100 g) or silica gel–plaster of Paris (90 g of silica gel, thoroughly mixed with 10 g of plaster of Paris) was added, with stirring. After stirring for a further 15 min, the solvent was removed on a water-bath under water-pump suction, avoiding exposure to light, so as to obtain a free-flowing powder. These preparations were stored in dark bottles.

The above preparations were slurried with water (2–2.5 parts) by gently rubbing in a pestle and mortar and plates (15 × 3.5 cm) were coated with the slurry with the aid of an applicator*, giving 0.5-mm layers. The plates were air-dried for *ca.* 4 h at room temperature and finally activated at 105° for 2.5 h and used after cooling in dry air for 10–15 min**.

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The olefin mixtures were applied and the plates developed as described earlier[1].

RESULTS AND DISCUSSION

It can be seen from Table I that for all the cases studied, the R_F values are higher in presence of gypsum. It can also be seen that for an isomeric pair the distance

* For details of the applicator, see ref. 1.

** These plates can be stored in a dark desiccator for 2–3 weeks, but must be activated at 105° for 30 min before use.

TABLE I

R_F VALUES OF DIFFERENT TERPENE OLEFINS ON SILVER ION–SILICA GEL PLATES WITH AND WITHOUT GYPSUM (PLASTER OF PARIS)

No.	*Compound**	*No. of olefinic bonds*	*Solvent***	R_F***			
				Silver nitrate		*Silver perchlorate*	
				With gypsum	*Without gypsum*	*With gypsum*	*Without gypsum*
1	Longicyclene	0	A	0.75	0.68	0.77	0.76
2	Isolongifolene	1	A	0.66	0.58	0.67	0.66
3	Longifolene	1	A	0.44	0.31	0.32	0.14
4	α-Gurjunene	1	B	0.82	0.80	0.79	0.78
5	α-Bergamotene	2	B	0.74	0.62	0.71	0.61
6	β-Bisabolene	3	B	0.37	0.18	0.32	0.16
7	α-Himachalene	2	C	0.69	0.56	0.70	0.55
8	β-Himachalene	2	C	0.61	0.46	0.62	0.46
9	Cembrene	4	D	0.85	0.81	0.86	0.83
10	Cembrene A	4	D	0.65	0.41	0.42	0.16
11	Unknown diterpene (compound X)	?	D	0.77	0.63	0.76	0.61

* Compounds 1–8 are sesquiterpene hydrocarbons ($C_{15}H_{24}$), while compounds 9–11 are diterpenes ($C_{20}H_{34}$).

** Solvent systems: A, light petroleum; B, 50% benzene in light petroleum; C, 20% benzene in light petroleum; D, 15% ethyl acetate in benzene.

*** Average of four experiments; temperature 25 ± 1°; solvent front, 10 cm. For a particular group (same solvent system) of olefins, a mixture of olefins was spotted.

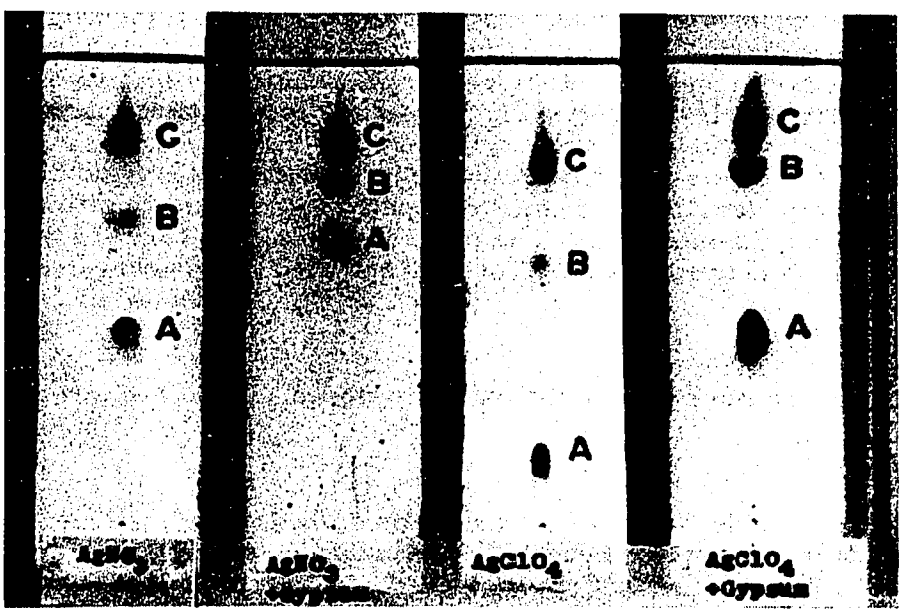

Fig. 1. Thin-layer chromatography of some diterpene hydrocarbons on silver ion layers prepared in four different ways. Compounds: A = Cembrene A; B = unknown diterpene (compound X); C = cembrene. Solvent, 15% ethyl acetate in benzene. Solvent front, 10 cm. Temperature, 25 ± 1°.

between the two spots in a developed plate, which is a measure of resolution[8], is always greater both for silver nitrate and silver perchlorate containing layers in the absence of gypsum (*cf.*, Fig. 1). It may be pointed out that normally a binder is considered not to affect the quality of separation (see, *e.g.*, ref. 9), although the solvent front is known to move more slowly on the addition of gypsum (see, *e.g.*, ref. 10). In the present investigations, however, it was noted that, as known earlier, the solvent front did move more slowly when gypsum was incorporated and the quality of separation was also adversely affected.

From the degree of separation for an isomeric pair, as calculated from Table I, it can be shown that weight for weight silver perchlorate definitely gives superior resolution in some instances while in others it is at least as good as silver nitrate. It may be further noted that silver perchlorate has a silver content of 52.1%, which is lower than the corresponding value (63.5%) for silver nitrate. Although it is known[11] that the stability of silver ion–olefin complexes is dependent on the counter negative ion and that silver perchlorate is superior to silver nitrate as a complexing agent, it is difficult at present to rationalize the differences in the behaviour of olefins as inferred from the results in Table I.

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