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Note

Reduction of terpenoids on thin-layer chromatographic plates

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Various organic reactions in a solid matrix are known to occur¹⁻⁴. Reduction of a mesylate or a tosylate constitutes as efficient method for the reductive elimination of the hydroxy group of a primary or secondary alcohol. Sodium amalgam is the classical reducing agent and lithium aluminium hydride usually gives good results, except with hindered alcohols⁵. Ringold and Bowers⁶ used sodium iodide in acetic acid with success to reduce an α -ketol to sylate with retention of the intact carbonyl group. A novel reduction of khusol mesylate with sodium iodide and acetic acid has also been reported⁷.

Stereospecific reduction of isolludin S and M with aluminium isopropoxide in chromatography on alumina has been reported⁸. Aluminium isopropoxide has also been used for the reduction of carbonyl compounds, particularly unsaturated alde-

TABLE I

R_F VALUES OF REACTION PRODUCTS OF TERPENOIDS WITH SODIUM IODIDE-ACETIC ACID ON SILICA GEL G PLATES

Solvent: benzene-ethyl acetate (10:1 and 11:1).

Compound	Original compound		Reaction product	
	10:1	11:1	10:1	11:1
4-Carene	0.79	0.81	0.59	0.62
Citral	0.59	0.61	0.33	0.39
Khusilal	0.64	0.65	0.74	0.76
α -Ionone	0.55	0.61	0.26	0.38
β -Ionone	0.45	0.53	0.35	0.39
Carvone	0.60	0.62	0.52	0.53
Zerumbone	0.53	0.63	0.28	0.37
Costunolide	0.51	0.52	0.61	0.62
Santonin	0.22	0.25	0.42	0.49
Dehydrocostus lactone	0.52	0.54	0.41	0.47
Daucol tosylate	0.70	0.72	0.37	0.48
Khusinol mesylate	0.67	0.72	0.75	0.78
Khusol mesylate	0.55	0.60	0.71	0.73
Khusilal phenylhydrazone	0.77	0.78	0.80	0.83
Khusinol benzoate	0.65	0.63	0.71	0.73
Isopulegol 3,5-dinitrobenzoate	0.77	0.78	0.50	0.52

TABLE II

R_F VALUES OF REACTION PRODUCTS OF TERPENOIDS WITH ALUMINIUM ISOPROPOXIDE

Meerwein-Verley-Ponndorf type reduction. Solvent: benzene-ethyl acetate (9:1 and 8:2).

Compound	Original compound		Reaction product	
	9:1	8:2	9:1	8:2
Δ -Carene	0.78	0.72	0.57	0.49
Citral	0.60	0.62	0.40	0.50
Khusilal	0.59	0.65	0.79	0.77
α -Ionone	0.60	0.69	0.34	0.46
α -ionone	0.56	0.63	0.31	0.48
Carvone	0.63	0.65	0.57	0.50
Zerumbone	0.61	0.67	0.40	0.43
Costunolide	0.56	0.66	0.33	0.50
Santonin	0.22	0.25	0.39	0.40
Dehydrocostus lactone	0.62	0.61	0.38	0.44
Daucol tosylate	0.67	0.62	0.42	0.27
Khusinol mesylate	0.70	0.65	0.56	0.51
Khusol mesylate	0.69	0.63	0.83	0.77
Khusilal phenylhydrazone	0.86	0.80	0.90	0.86
Khusinol benzoate	0.75	0.71	0.60	0.54
Isopulegol 3,5-dinitrobenzoate	0.73	0.64	0.40	0.42

TABLE III

R_F VALUES OF THE REACTION PRODUCTS OF TERPENOIDS WITH SODIUM BOROHYDRIDE ON SILICA GEL G PLATES

Solvent: benzene-ethyl acetate (10:1 and 8:2)

Compound	Original compound		Reaction product	
	10:1	8:2	10:1	8:2
Δ -Carene	0.79	0.73	0.59	0.50
Citral	0.65	0.67	0.50	0.53
Khusilal	0.66	0.72	0.75	0.78
α -Ionone	0.60	0.65	0.42	0.57
β -Ionone	0.58	0.63	0.41	0.44
Carvone	0.61	0.69	0.40	0.47
Zerumbone	0.65	0.75	0.20	0.36
Costunolide	0.59	0.70	0.54	0.65
Santonin	0.28	0.25	0.37	0.34
Dehydrocostus lactone	0.70	0.71	0.41	0.61
Daucol tosylate	0.75	0.67	0.42	0.54
Khusinol mesylate	0.65	0.64	0.46	0.51
Khusol mesylate	0.57	0.68	0.82	0.85
Khusilal phenylhydrazone	0.77	0.80	0.80	0.86
Khusinol benzoate	0.77	0.75	0.36	0.51
Isopulegol 3,5-dinitrobenzoate	0.69	0.64	0.42	0.41

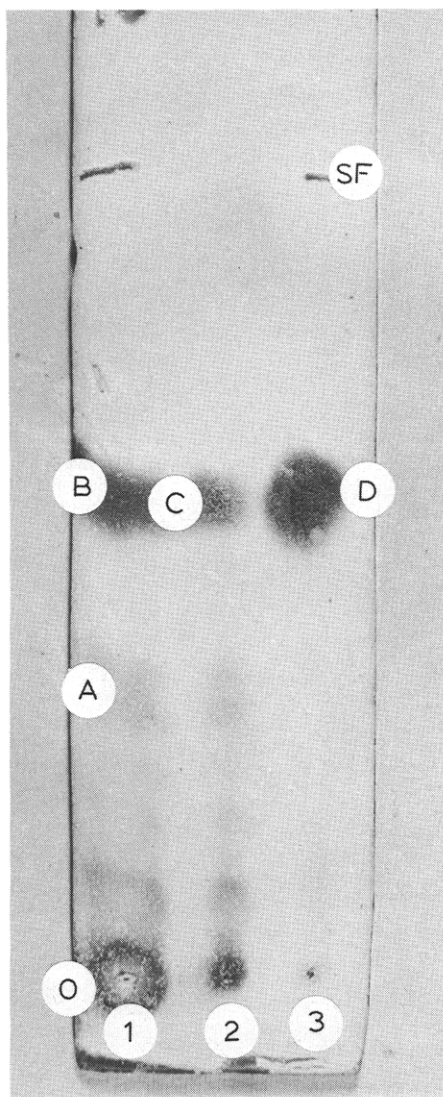
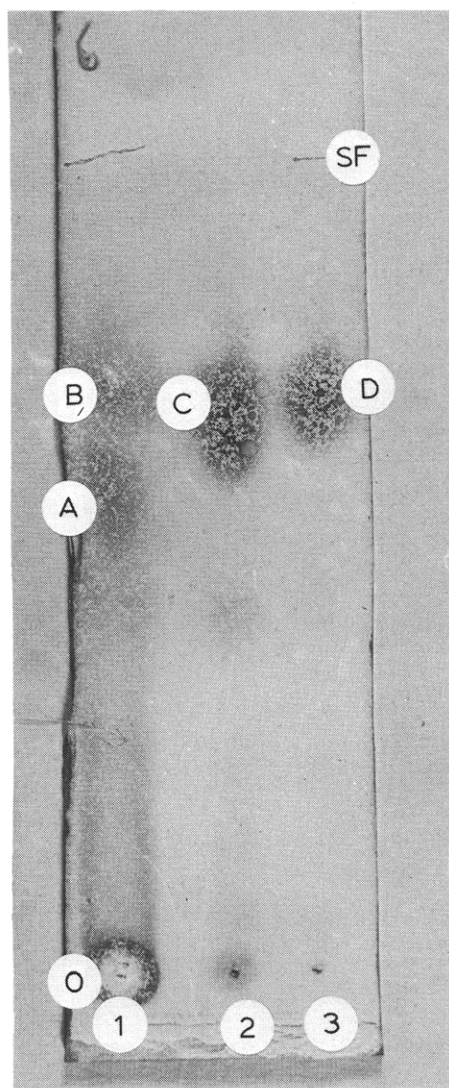


Fig. 1. Chromatogram obtained after reduction of zerumbone using sodium iodide and acetic acid. A, Product of reduction; B, unreacted zerumbone; C, zerumbone after 24 h on active surface; D, zerumbone at room temperature. SF, Solvent front; O, origin.

Fig. 2. Chromatogram obtained after reduction of dehydrocostus lactone using sodium iodide and acetic acid. A, Product of reduction; B, unreacted dehydrocostus lactone; C, dehydrocostus lactone after 24 h on active surface; D, dehydrocostus lactone at room temperature. SF, Solvent front; O, origin.

hydres and ketones, as the reagent attacks only carbonyl compounds. An example is the reduction of crotonaldehyde to crotyl alcohol⁹.

A widely used method^{10,11} for the synthesis of nitroalkenes involves sodium borohydride reduction of conjugated nitroalkenes, synthesized by nitromethylation^{12,13} of aliphatic or aromatic aldehydes. Reduction of a variety of

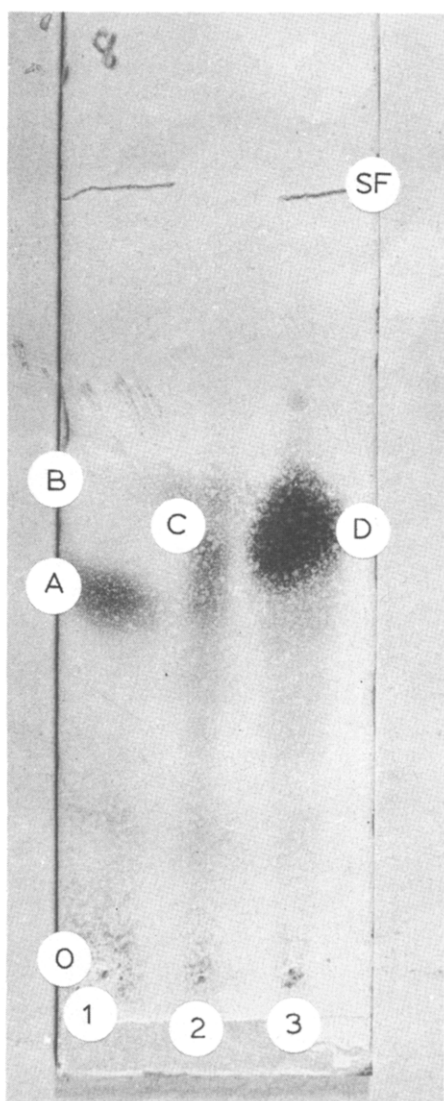
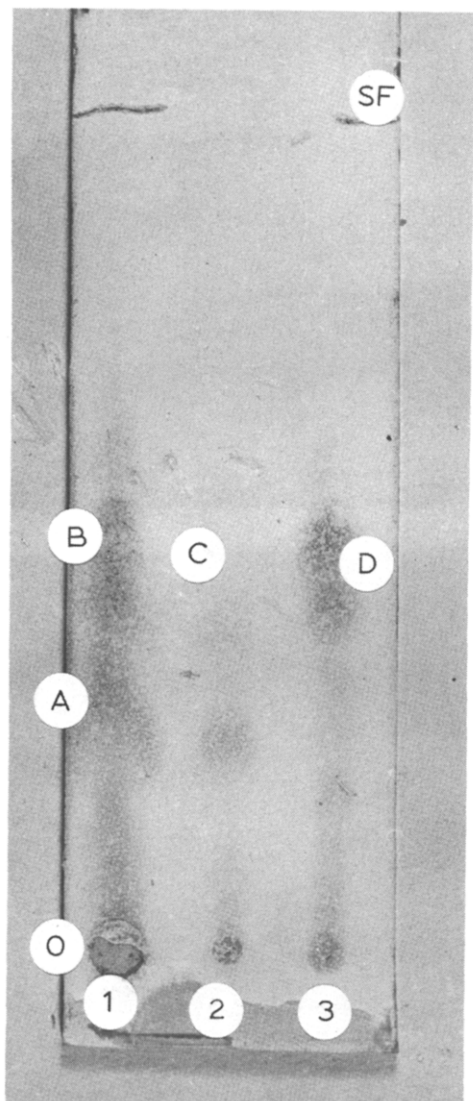


Fig. 3. Chromatogram obtained after Meerwein-Verley-Ponndorf type reduction of β -ionone using aluminium isopropoxide. A, Product of reduction; B, unreacted β -ionone; C, β -ionone after 24 h on active surface; D, β -ionone at room temperature. SF, Solvent front; O, origin.

Fig. 4. Chromatogram obtained after Meerwein-Verley-Ponndorf type reduction of α -ionone using aluminium isopropoxide. A, Product of reduction; B, unreacted α -ionone; C, α -ionone after 24 h on active surface; D, α -ionone at room temperature. SF, Solvent front; O, origin.

nitrostyrenes with sodium borohydride in the presence of silica gel in a mixture of chloroform and 2-propanol has been reported¹⁴.

El-Maghraby¹⁵ carried out chemical reactions on thin-layer chromatographic (TLC) plates in order to solve several problems, particularly involving natural products. The amounts of materials obtainable from natural sources are often too small

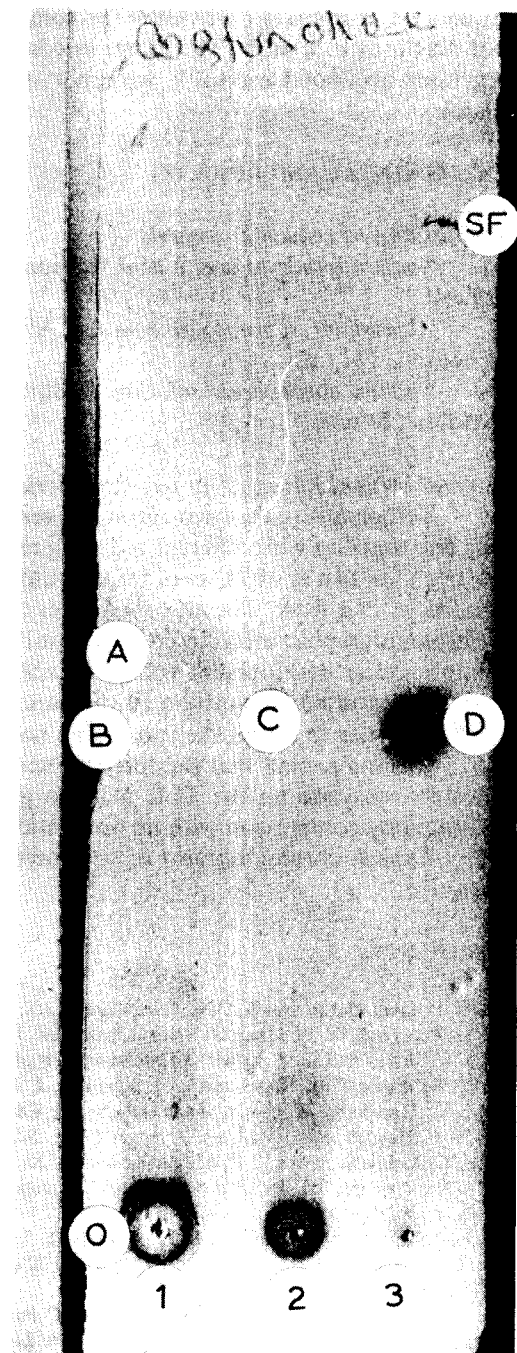
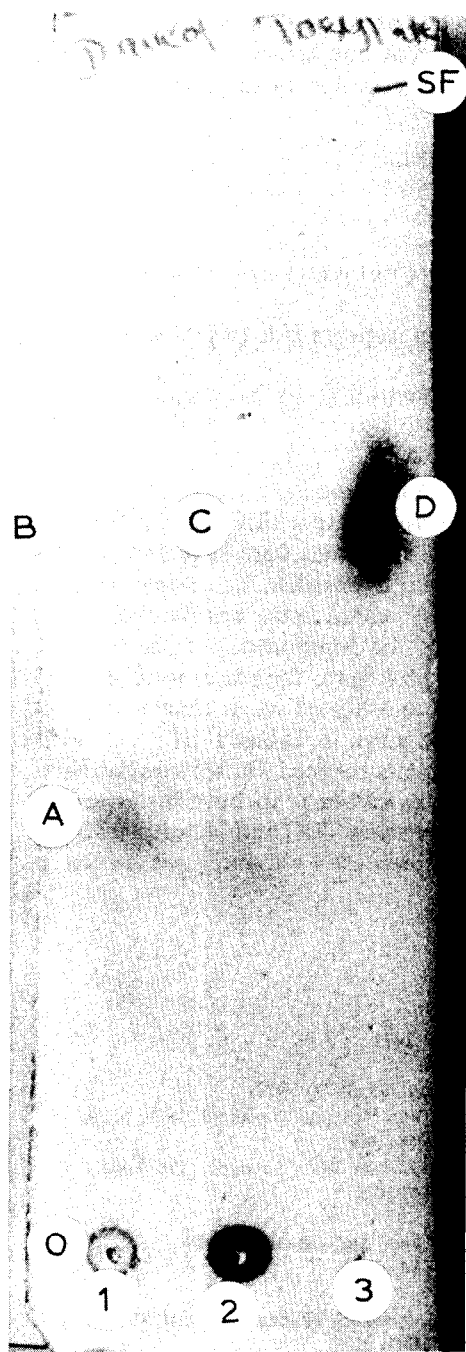


Fig. 5. Chromatogram obtained after reduction of daucol tosylate using sodium borohydride. A, Product of reduction; B, unreacted daucol tosylate; C, daucol tosylate after 24 h on active surface; D, daucol tosylate at room temperature. SF, Solvent front; O, origin.

Fig. 6. Chromatogram obtained after reduction of costunolide using sodium borohydride. A, Product of reduction; B, unreacted costunolide; C, costunolide after 24 h on active surface; D, costunolide at room temperature. SF, Solvent front; O, origin.

to be able to prepare derivatives for comparison with known products or to carry out reactions in a flask. Therefore, in constitution of our earlier studies of organic reactions in a solid matrix¹⁶, we report here the reduction of terpenoids on TLC plates.

EXPERIMENTAL AND RESULTS

Preparation of reducing reagents

Sodium iodide in acetic acid. Sodium iodide (5 g) was dissolved in acetic acid (25 ml).

Aluminium isopropoxide solution. Aluminium isopropoxide (5 g) was dissolved in benzene (20 ml).

Sodium borohydride solution. Sodium borohydride (5 g) was dissolved in dry pyridine (20 ml).

General method for carrying out the reaction on TLC plates

Terpenoids in the appropriate solvent were applied to a TLC plate at the starting line together with different reducing reagents. The plates were heated in an electric oven for 24 h at 110°C in order to simulate, as far as possible, the normal reaction conditions in a flask. The adsorbed layer was then treated in the normal manner as a chromatographic medium for the resolution of the components of the reaction mixture. After development with a suitable solvent system, the plates were sprayed with concentrated sulphuric acid-methanol (1:1) and heated in an electric oven at 110°C in order to reveal the spots. The results are given in Tables I-III.

It is interesting that the three reducing reagents reduced khusol mesylate and khusinol mesylate on the TLC plate to give (-)- γ -cadinene in both instances, as indicated by comparison with an authentic sample using TLC and IR spectroscopy.

Typical chromatograms of terpenoids obtained after reduction are shown in Figs. 1-6.

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