

Note

Chemical dehydrogenation in a solid matrix

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A number of organic reactions in a solid matrix are known to occur¹⁻⁵. For example, El-Maghraby⁶ carried out chemical reactions on chromatoplates in order to solve several problems, particularly involving natural products. This technique is very useful in biosynthetic and industrial studies where the material is available in such a small amount that it is not possible to derivatize it for comparison with known compounds or to subject them to any reactions in a flask. Therefore, in continuation of our earlier studies^{7,8} on organic reactions in a solid matrix, we report here the dehydrogenation of terpenoids with the mixed dehydrogenating reagent 1,4-naphthoquinone-potassium *tert.*-butoxide.

EXPERIMENTAL

Preparation of chromatoplates

Glass plates (5 × 20 cm) were coated with silica gel G slurry, which was prepared by mixing thoroughly one part by weight of silica gel G with two parts by volume of water. After drying in air, the plates were heated in an oven for 30 min at 110°C and stored.

*Preparation of potassium *tert.*-butoxide*

Potassium metal was cut under xylene and dried over sodium wire in a mortar. The mortar containing the scraps of metal was moved to the rear of the hood and *tert.*-butyl alcohol added in small proportions with the help of a dropper. Sufficient *tert.*-butyl alcohol was added to ensure complete decomposition of all the potassium occurred⁹.

General method for carrying out the reaction on chromatoplates

The terpenoids (4 µg) in light petroleum (b.p. 40-60°C) were applied to the plate at the starting line together with dehydrogenating reagent (1,4-naphthoquinone-potassium *tert.*-butoxide). The plates were heated in an electric oven for 24 h at 120°C in order to simulate as far as possible the normal reaction conditions in a flask. The adsorbed layer was then treated as in thin-layer chromatography: after development with a suitable solvent system (benzene-ethyl acetate, 10:1 and 4:1) the plates were sprayed with concentrated sulphuric acid-methanol (1:1) and heated in an electric oven at 110°C for 5 min in order to reveal the spots. The R_F values were calculated.

TABLE I

R_F VALUES OF REACTION PRODUCTS OF TERPENOIDS WITH 1,4-NAPHTHOQUINONE-POTASSIUM *TERT.*-BUTOXIDE ON SILICA GEL G PLATES

Solvent system: benzene-ethyl acetate (10:1 and 4:1).

Compound	R_F value		Reaction product	
	Original compound		10:1 4:1	
	10:1	4:1	10:1	4:1
Khusinol	0.52	0.62	0.78	0.87
Khusol	0.58	0.60	0.58	0.60
Isopulegol	0.47	0.48	0.63	0.63
Daucol	0.35	0.35	0.59	0.64
Equol	0.29	0.29	0.01	0.09
Linalool	0.22	0.22	0.26	0.29
Menthol	0.49	0.52	0.72	0.79
Citranellol	0.51	0.52	0.35	0.35
Methyleugenol	0.63	0.64	0.57	0.60
Khusilal	0.85	0.84	0.72	0.72
Citral	0.45	0.43	0.05	0.06
Carvone	0.23	0.24	0.23	0.24
Abietic acid	0.36	0.38	0.46	0.48
Santonin	0.34	0.21	0.33	0.35
Khusinol benzoate	0.61	0.61	0.69	0.70

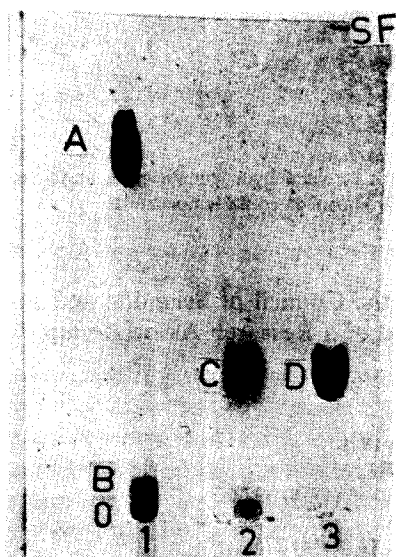


Fig. 1. Dehydrogenation of costunolide on chromatoplates. A, Major product of dehydrogenation; B, minor product of dehydrogenation; C, costunolide (blank experiment) at reaction temperature after 48 h; D, costunolide at room temperature.

RESULTS AND DISCUSSION

The results obtained for various terpenoids are given in Table I. Chemical dehydrogenation was carried out on inert thin-layer chromatographic plates under controlled conditions. It appears that the application of 1,4-naphthoquinone-potassium *tert.*-butoxide in an inert chromatographic adsorbent within the usual area of the spot can produce results comparable to those obtained in a conventional reaction apparatus. However, certain terpenoids were only partially dehydrogenated using this reagent. Further, the method we have employed is simpler and permits better reactions than the procedures cited and is completely reproducible. It is a useful technique as it requires only very small amounts of material (4 μg). Typical chromatograms of terpenoids obtained after dehydrogenation are shown in Figs. 1 and 2.

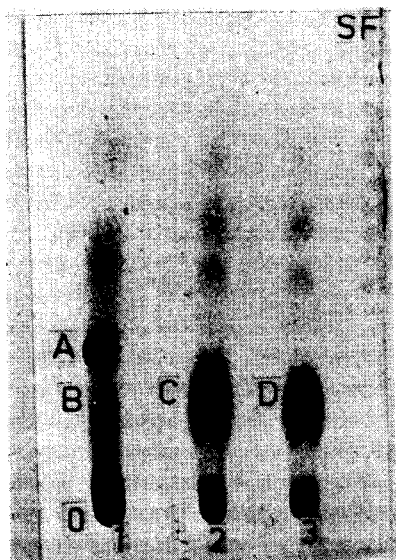


Fig. 2. Dehydrogenation of khusol on chromatoplates. A, Product of dehydrogenation; B, unreacted khusol; C, khusol (blanc) at reaction temperature after 24 h; D, khusol at room temperature.

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REFERENCES

- 1 N. P. Damodaran and S. Dev, *Tetrahedron Lett.*, 28 (1963) 1941.
- 2 H. Pines and W. O. Haag, *J. Am. Chem. Soc.*, 82 (1960) 2471.
- 3 Y. M. Fung, P. de Mayo and J. H. Schauble, *J. Org. Chem.*, 43 (1978) 3977.
- 4 R. Ikan, *J. Chromatogr.*, 17 (1965) 591.
- 5 R. Ikan, J. Kashman and E. D. Bergmann, *J. Chromatogr.*, 14 (1964) 275.
- 6 M. A. El-Maghraby, *J. Indian Chem. Soc.*, 54 (1977) 401.
- 7 K. K. Badaisha and J. C. Kohli, *J. Chromatogr.*, 268 (1983) 549.
- 8 J. C. Kohli, K. K. Badaisha and V. K. Gautam, *J. Chromatogr.*, 288 (1984) 489.
- 9 L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis*, Vol. 1, Wiley, Chichester, New York, 1967.