The Tritylone Protecting Group: Ether Cleavage by Wolff-Kishner Reduction

By William E. Barnett* and Larry L. Needham

(Chemistry Department, University of Georgia, Athens, Georgia 30601)

Summary Alcohols react readily with 9-phenyl-9-hydroxyanthrone to form substituted trityl ethers which can be readily cleaved by a specific base-catalysed reaction, the Wolff-Kishner reduction.

TRITYL ethers are stable to a wide variety of reagents but are easily cleaved by dilute acid or by hydrogenolysis in neutral media.^{1,2} The trityl group (I) can be easily attached to produce trityl ethers from most primary and some secondary alcohols.² Because of these properties, the trityl group is one of the most important protecting groups for hydroxy-functions. As a complement to the trityl group it would be desirable to have a trityl derivative which could be cleaved under basic conditions. The general utility of such a derivative would be enhanced if the group were stable to the majority of base-catalysed reactions but could be cleaved by a specific one. The tritylone group (II) is such a group.

In principle, a trityl derivative such as (IV) should be cleaved by the Wolff-Kishner reduction.^{3,4} The accepted mechanism⁵ of that reaction involves conversion of the carbonyl carbon atom into a carbanionic centre, leading to elimination in cases where ketones have good leaving groups on the α -carbon atom.^{6,7} It was expected that a phenyl ring between the carbonyl carbon atom and the carbon atom bearing the leaving group would still permit elimination. Of the types of monocarbonyl systems (III) considered, the particular system (IV) would lead by elimination of OR⁻ to a stable by-product, 9-phenylanthracene (VI). In practice, this method is a very efficient one for cleaving tritylone ethers (IV). From the Wolff-Kishner reduction³ of n-hexadecanyl tritylone ether, n-hexadecanol is recovered almost quantitatively and 9-phenylanthracene can be isolated in very good yield.

A desirable property for any protecting group is that it can be easily attached. Several methods for attaching the tritylone group have been studied. The ethers (Table)[†]

ROH	Yield of tritylone ether (%)	M.p. of ether (° C)
Hexadecanol	 88	63 - 64
Dodecanol	 86	53 - 54
Octan-2-ol	 75	4445
Cholesterol	 59	204 - 206
Cyclohexanol	 55	170-171

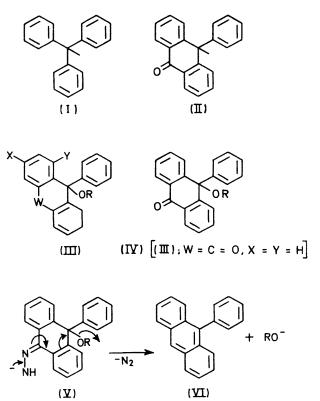
have been prepared using our best method. One equivalent of the alcohol and one equivalent of tritylone alcohol^{8,9} are heated under reflux for 10-20 h in a C₆H₆ solution containing a catalytic amount of toluene-p-sulphonic acid. Water, which distils over as the C_6H_6 azeotrope, is collected in a Dean-Stark trap. The yields reported are based on the amount of pure ether isolated after chromatography on neutral alumina.

† All new compounds gave satisfactory analytical and spectral data.

- ¹ A. Baeyer, Ber., 1909, 42, 2625. ² B. Helferich, "Trityl Ethers of Carbohydrates" in Adv. Carbohydrate Chem., 1948, vol. 3.

- ⁵ B. Henferich, Thilf Ethers of Carbonydrates in Adv. Carbonydrate Chem., 1948, vol. 5.
 ⁵ Huang-Minlon, J. Amer. Chem. Soc., 1946, 68, 2487.
 ⁴ D. Todd in "Organic Reactions", Wiley, New York, 1948, vol. 4.
 ⁵ H. H. Szmant and M. N. Roman, J. Amer. Chem. Soc., 1966, 88, 4034, and references therein.
 ⁶ P. S. Wharton, S. Dunny, and L. Soto Krebs, J. Org. Chem., 1965, 27, 2960.
- ⁷ N. J. Leonard and S. Gelfand, J. Amer. Chem. Soc., 1955, 77, 3269.
 ⁸ R. O. C. Norman and W. A. Waters, J. Chem. Soc., 1958, 167.
- ⁹ F. F. Blicke and R. D. Swisher, J. Amer. Chem. Soc., 1934, 56, 1406.

We thank the Petroleum Research Fund and the office of General Research at the University of Georgia for support of this work.



(Received, November 24th, 1970; Com. 2034.)