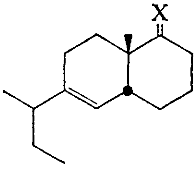
2,4-Dinitrophenylhydrazones as Carbonyl-protecting Groups during Hydroboration

By JOHN E. MCMURRY

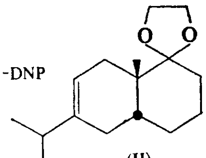
(*Division of Natural Sciences, University of California, Santa Cruz, California,* 95060)

DURING some synthetic work, we needed to transform the keto-olefin, (Ia), stereospecifically into the saturated ketol, (IIIa). Not surprisingly,[1] hydroboration with one-half equivalent BH_3 resulted in preferential reduction of the carbonyl, rather than of the olefinic double bond. Ketalization of the carbonyl to protect it unfortunately also caused simultaneous double bond migration [(I) → (II)] under the necessary acidic conditions. Although the steric reasons for equilibrium double bond positions in such octalins are far from clear,[2] it seems that C(1) must remain trigonal in order for the double bond to be most stable in the 5,6-position.† There are, however, no known groups which protect a carbonyl toward hydroboration, yet which keep the carbonyl carbon trigonally hybridized. Oximes[3] and oxime acetates,[4] for instance, are reported to be reduced upon treatment with BH_3. The reaction of BH_3 with hydrazones, however, does not seem to have been reported.

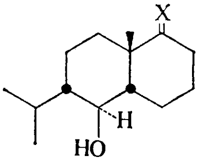
When the 2,4-dinitrophenylhydrazone, (Ib),‡ m.p. 120—121°, was treated with one-half equivalent BH_3 under the usual conditions, and the resulting dialkylborane intermediate was then treated with basic hydrogen peroxide, attack occurred on the olefinic double bond most distant from the convex face of the *cis*-octalin to give alcohol (IIIb),‡ m.p. 196—197°, in 65% yield. This structural assignment follows from the spectral and analytical data {mass spectrum: P^+ 404; i.r.: 3610 (O–H), 3350 (N–H), 1610, 1590, 1550; n.m.r.: τ 0·8—2·3 [3H, typical aromatic 2,4-dinitrophenylhydrazone (DNP) pattern], 6·65 (1H, J 9 c./sec.), 8·70 (3H,)s, 9·25 and 9·35 (6H, two doublets, J 7 c./sec.)}. Thus the 2,4-DNP moiety was not attacked and seems relatively stable to BH_3. Ozonolysis in ethyl acetate at −78° removed the protecting group,[5] and the desired ketol (IIIa), was obtained in 50% overall yield from olefin (Ia).



(Ia) X=O
(Ib) X=2,4-DNP



(II)



(IIIa) X=O
(IIIb) X=2,4-DNP

There are few synthetic stiuations where this method of carbonyl protections is necessary; however, for those situations, it is now available and useful.

We thank the Petroleum Research Fund of the American Chemical Society for their support of this work.

(*Received, February 26th,* 1968; *Com.* 224.)

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† Thus in (Ia) an equilibrium mixture of double bond isomers contains ~75% Δ,^{5,6} ~25% $\Delta^{6,7}$. In the ketal (III), where C(1) is tetrahedral, the equilibrium double bond position is $\Delta^{6,7}$ by >90%. In the corresponding 1αH, 1β-acetoxy-compound, where C(1) is again tetrahedral, an equilibrium mixture of olefins has ~70% $\Delta^{6,7}$, ~30% $\Delta^{5,6}$.

‡ Satisfactory spectral and analytical data were obtained for this compound.

[1] H. C. Brown and W. Korytnyk, *J. Amer. Chem. Soc.*, 1960, **82**, 3866.

[2] L. F. Fieser and M. Fieser, "Steroids", Reinhold, New York, 1959, p. 276.

[3] H. Feuer, B. F. Vincent, jun., and R. S. Bartlett, *J. Org. Chem.*, 1965, **30**, 2877.

[4] A. Hassner and P. Catsoulacos, *Chem. Comm.*, 1967, 590.

[5] According to the procedure of G. A. Fleisher and E. C. Kendall, *J. Org. Chem.*, 1951, **16**, 556.