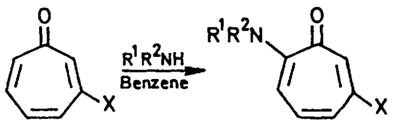
Regiospecific Amination of Deactivated Cycloheptatrienones *via* Hydride Replacement

By BRUNO RICCIARELLI, RENZO CABRINO, FRANCESCO DEL CIMA, C. ALBERTO VERACINI, and FRANCESCO PIETRA*
(*Department of Chemistry, Università di Pisa,* 56100 *Pisa, Italy*)

Summary 3-Dialkylaminotropones and 3-alkoxytropones can be regiospecifically aminated at C-7 with either primary or secondary amines in benzene, whilst 3-alkylaminotropones resist amination.

AMINATION of the cycloheptatrienone nucleus *via* hydride replacement is synthetically interesting,[1] though of limited application. Examples are restricted to reactions of cycloheptatrienone with nucleophilic reagents either possessing strong reducing properties, such as aminocupric complexes[2] and hydrazine,[3] or capable of undergoing competitive fragmentation, such as hydrazine itself, in which nuclear hydrogen is thought to be transferred as a proton.[4] Information concerning hydride replacements, in basic media, particularly when no strong reducing agents are available, is scarce.[5]



(1) (2)

a, $X = NMe_2$
b, $X = NC_5H_{10}$
c, $X = OMe$

a; $R^1 = R^2 = Me$; $X = NMe_2$
b; R^1, $R^2 = C_5H_{10}$; $X = NC_5H_{10}$
c; $R = Bu^n$, $R^2 = H$; $X = OMe$

We now report a novel nuclear amination of 3-dialkylaminotropones and 3-alkoxytropones under mild, non-reductive conditions. Thus, 3-dimethylaminotropone (**1a**), 0·1 M, was treated with dried dimethylamine, 7·5 M, in dried benzene at room temperature for 15 h to give, after solvent evaporation and sublimation, 3,7-di-dimethylaminotropone (**2a**), m.p. 90°, in 45% yield,[†] no isomeric product being detectable by chromatography of the reaction mixture.

The generality of the method is shown by the formation of 3,7-di-piperidinotropone (**2b**), and by amination of (**1a**) with primary amines along similar lines.

Because of the similar electronic nature of alkoxy and dialkylamino groups, we also attempted amination of 3-alkoxytropones. Compound (**2c**), m.p. 38—41° was obtained in *ca.* 50% yield from (**1c**) and n-butylamine in benzene.

In contrast, 3-alkylaminotropones, such as 3-n-butylaminotropone, resist amination by either primary or secondary amines in benzene; prolonged heating of the mixture only leads to tarry materials.

These aminations are useful because of their complete regiospecificity giving troponoids unavailable by any other route, and the synthetic versatility of the amino function.[1] The ease of amination is surprising because of the electron donating properties of the dialkylamino and alkoxy substituents on (**1**). Amination of (**1c**) is particularly surprising because (**1c**) reportedly resist aminations by hydrazine[6] whilst 2-methoxytropone is known to undergo easy replacement of the methoxy group by amines in benzene.[7] We suggest that hydride transfer occurs to a molecule of unreacted cycloheptatrienone and that 3-alkylaminotropones are unreactive because of the acidity of their amino hydrogen.

Financial support by C.N.R., Roma, is acknowledged.

(*Received*, 1*st July* 1974; *Com.* 783.)

[†] Structures of new products are supported by analysis and u.v., i.r., n.m.r., and mass spectra. In particular, structure (**2a**) is supported by the nuclear Overhauser effect on irradiation at the methyl resonances.

[1] F. Pietra, *Chem. Rev.*, 1973, **73**, 293.
[2] K. Kikuchi, *Bull. Chem. Soc. Japan*, 1967, **40**, 385.
[3] E. Zbiral, J. Jaz, and F. Wessely, *Monatsh.*, 1961, **92**, 1154; E. Zbiral, F. Takacs, and F. Wessely, *ibid.*, 1964, **95**, 402.
[4] G. L. Buchanan and R. D. Lockart, *J. Chem. Soc.*, 1959, 3586; T. Mukai, H. Tsuruta, and T. Nozoe, *Tetrahedron Letters*, 1966, 1063.
[5] N. C. Deno, H. J. Peterson, and G. S. Saines, *Chem. Rev.*, 1960, **60**, 7; A. I. Shatenshtein, 'Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds,' Consultants Bureau, New York, 1962, p. 248—253; G. A. Hamilton, in 'Progress in Bio-organic Chemistry,' ed. Kaiser and Kezdy, Wiley-Interscience, 1971, p. 85—157.
[6] T. Nozoe, in 'Non-Benzenoid Aromatic Compounds,' ed. D. Ginsburg, Interscience, New York, 1959, p. 416.
[7] F. Pietra and F. Del Cima, *J. Chem. Soc.* (*B*), 1971, 2224; G. Biggi, F. Del Cima, and F. Pietra, *J. Amer. Chem. Soc.*, 1973, **95**, 7101.

Printed by Heffers Printers Ltd Cambridge England