The Adduct of 2-Methoxytropone and Sodium Methoxide: a Flattened, Conjugated Seven-membered Ring with Tetrahedral Carbon

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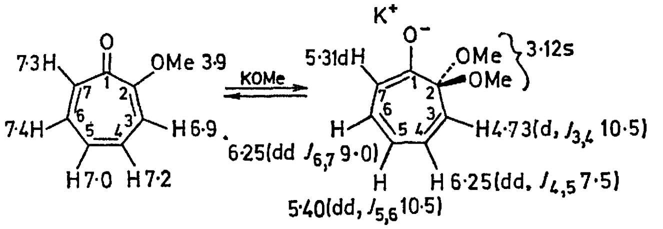
Summary The first stable adduct from a nucleophile, potassium methoxide, and a *deactivated* cycloheptatrienone, 2-methoxytropone, has a flattened *gem*-dialkoxy-structure, whilst adducts at an unsubstituted carbon, such as those from methoxide with tropone, are short-lived species.

On mixing of distilled 2-methoxytropone and KOMe in dried 3:1 Me_2SO–MeOH under N_2 at room temperature equilibrium (1) is rapidly established. Formation of (2) is practically complete with (1) (0·03M) with a two-fold molar excess of methoxide. On neutralization, (2) reverts immediately to (1).

The structural assignment of (2) rests, as indicated in equation (1), on both 100 and 60 MHz ^1H n.m.r. spectra. All protons in (2) which show the correct integration, have been assigned unambiguously on the basis of both the ^1H n.m.r. spectra of analogues of (2) prepared from 2-methoxy-[3,5,7-$^2H_3$]tropone[1] and double resonance experiments on the equilibrium mixture. Irradiation at δ 6·25 changes the multiplets at δ 4·73, 5·40, and 5·31 into singlets.

Formation of (2) was unexpected since reaction of methoxide with 2-methoxytropone in methanol was reported previously to give methyl benzoate in high yield.[2] It is also remarkable that a deactivated cycloheptatrienone like (1) gives rise to an adduct by nucleophilic attack at C(2) rather than at C(7), as is the case with cycloheptatrienones possessing activating substituents at C(2).[3] Apart from deactivation of C(7) in (1), stabilization of C(2) in (2) by two electronegative groups[4] may be important in causing equilibrium (1) to favour formation of (2). In fact, interaction of methoxide with a non-deactivated substrate like tropone produces an adduct, presumably by attack at the α-carbon, as shown by a strong u.v. absorption around 360 nm. Polymerization is so rapid that the n.m.r. spectrum could not be recorded. Finally, both the occurrence of the u.v. absorption of (2) (λ_{max} 367 nm, log ϵ 3·8) at much longer wavelength than in tropone ethylene acetal (λ_{max} *ca.* 258 nm)[5] and the pronounced upfield shifts of 5-H, 7-H, and 3-H of (2) (5-H appearing more than 1 p.p.m. upfield from the value for the corresponding proton in cycloheptatriene,[6]) indicate strong delocalization of the negative charge of (2). This implies a very flattened conformation for (2) which is again remarkable in view of the ring strain introduced by a tetrahedral carbon.[7] Calculations on the last point, as well as on the possibility that the upfield shift of 3-H could be due in part to a norcaradiene form, are under way.



(1)

(1) (2)

δ values for (**1**) *and* (**2**); *J values in* Hz.

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