A New Stereospecific *trans*-Elimination of 2-Alkoxy- and 2-Cycloalkoxytropones to Alkenes and Cycloalkenes: the first Verification of the $[{}_s8_\pi + {}_a2_\sigma + {}_s2_\sigma]$ Process

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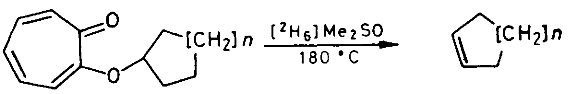
Solutions of 2-alkoxy- and 2-cycloalkoxy-tropones were heated to give alkenes and cycloalkenes respectively, without skeletal rearrangement, in good yields; deuterium labelling studies confirmed a stereospecific *trans*-elimination, in a $[{}_s8_\pi + {}_a2_\sigma + {}_s2_\sigma]$ mode, with an interesting isotope effect and a large rate retardation.

Recently, we have observed the formation of a terminal diene by heating 2-(allyloxy)tropones.[1] We report herein a new thermal reaction of troponoid ethers, *i.e.*, the conversion of alkoxytropones into alkenes.

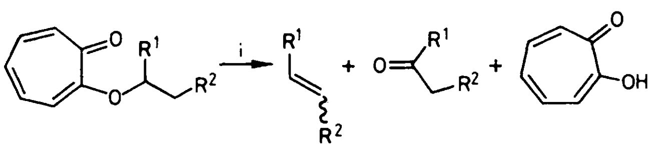
When 2-(cyclopentyloxy)tropone (**1a**)[2] was heated in $[^2H_6]Me_2SO$ at 180 °C (in a sealed tube) for 2 h, in the hope of obtaining cyclopentanone,[3] unexpected formation of cyclopentene (**2a**) together with tropolone (**3**) occurred as shown by n.m.r. spectroscopy. This contrasted with our earlier work, *e.g.*, heating 2-isopropoxytropone (**4a**) gave acetone (**5a**) and (**3**)[3] and prompted us to investigate similar reactions of other alkoxy- and cycloalkoxy-tropones. The treatment of alkoxytropones indeed formed mixtures of alkenes and alkanones; heating (**4b**) in $[^2H_6]Me_2SO$ at 180 °C for 30 min† gave *Z*- and *E*-but-2-enes [*Z*- and *E*-(**6b**) 1:1] and butan-2-one (**5b**). Similar treatment of (**4c**) gave *Z*- and *E*-pent-2-enes [*Z*- and *E*-(**6c**)] and pentan-3-one (**5c**) (Scheme 1). Conversely, all the cycloalkoxytropones examined including 2-(cyclododecyloxy)-tropone (**1e**), a macrocyclic derivative, gave only the corresponding cycloalkene in a good yield.

Heating, as above, of the cyclo-octyl phenyl ether (**8**) had no effect and therefore the presence of an adjacent carbonyl group is essential for the elimination to occur. The ethers derived from 3,5,7-trimethyltropolone and 4-isopropyltropolone gave similar products to those from ethers of (**3**) which suggested the generality of this elimination in tropolonyl ethers. In addition, mass spectrometric and ^1H and ^{13}C n.m.r. analyses‡ of the purified (**3**) generated by heating 2-{*Z*-[2-$^2H_1$]-cyclo-octyloxy}tropone *Z*-[$^2H_1$]-(**1d**),[5] 2-{*E*-[2-$^2H_1$]cyclo-octyloxy}tropone *E*-[$^2H_1$]-(**1d**), and 2-{[2,2,8,8,-$^2H_4$]cyclo-octyloxy}tropone [$^2H_4$]-(**1d**) in decalin showed it to contain no



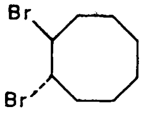
(**1**)
a, n = 1
b, n = 2
c, n = 3
d, n = 4
e, n = 8

(**2**)
a, (70%)
b, (85%)
c, (95%)
d, (95%)
e, (95%)

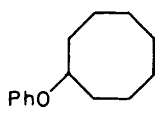


(**4a–c**) (**6a–c**) (**5a–c**) (**3**)

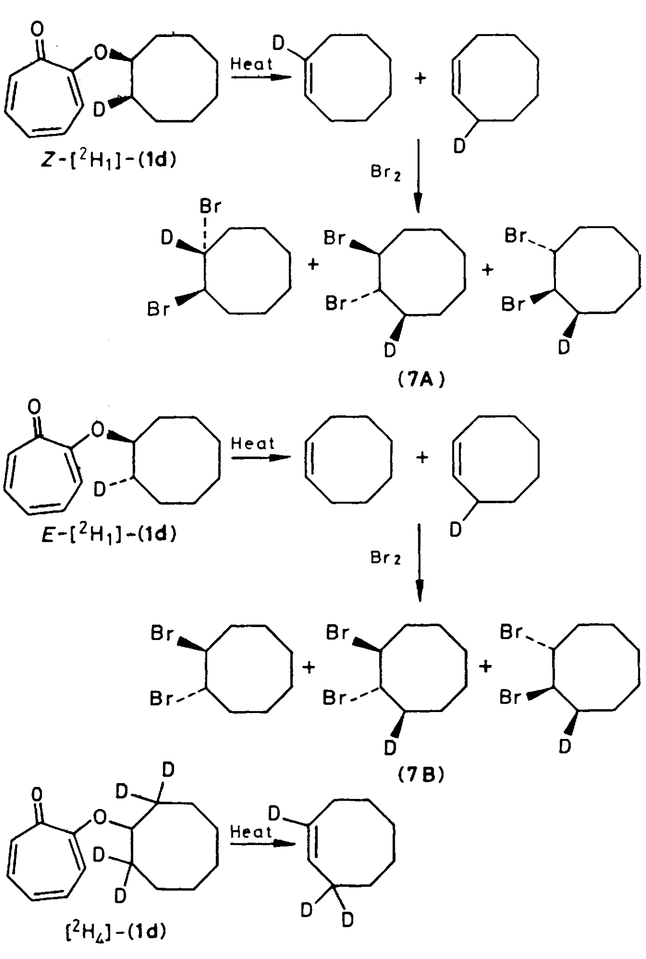
Scheme 1. *Reagents and conditions:* i, $[^2H_6]Me_2SO$, 180 °C; **a**, R^1 = Me, R^2 = H; **b**, R^1 = Me, R^2 = Me; **c**, R^1 = Et, R^2 = Me.



(**7**)



(**8**)



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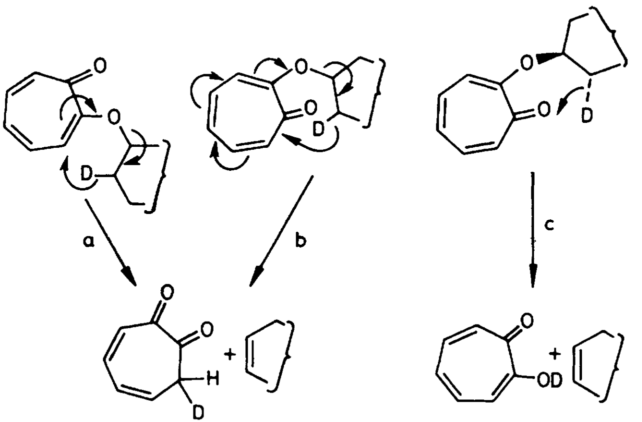
† For the lower alkoxytropones the reactions were carried out in sealed n.m.r. tubes. Although isolated yields of these products were poor owing to their volatility, we are confident that, based on the n.m.r. analyses, actual yields are almost quantitative. For the undetectability of propene from isopropoxytropones in the reaction with Me_2SO, we have no explanation other than a steric effect.

‡ Analogous to phenols, tropolones cause hydrogen-exchange in various polar or protic solvents. Heating (**3**) in $[^2H_6]Me_2SO$ at 180 °C caused a considerable incorporation of deuterium after 4 h, $[^2H_0]:[^2H_1]:[^2H_2]:[^2H_3]$ = 29:44:13:4. However, similar treatment of $[3,5,7\text{-}^2H_3]$-(**3**) in dioxan and decalin caused no exchange of the deterium (unpublished work in our laboratory).



Scheme 2

deuterium. Thus, possible $[2_\pi + 2_\sigma + 2_\sigma]$ and $[8_\pi + 2_\sigma + 2_\sigma]$ processes (Scheme 2, routes a and b respectively) should be rejected. The mass spectra of the deuteriodibromocyclo-octanes in the mixture from *Z*-$[^2H_1]$-(**1d**) {*m/z*, 283, 285, and 287 (1:2:1) for $[^2H_1]$-(**7A**); *m/z* 282, 284, and 286 for $[^2H_0]$-(**7A**) being negligible}, and in (**7B**) from *E*-$[^2H_1]$-(**1d**) {*m/z*, 282, 284, and 286 (1:2:1) for $[^2H_0]$-(**7B**); 283, 285, and 287 (1:2:1) for $[^2H_1]$-(**7B**). $[^2H_0]:[^2H_1] = 1:2$} obtained by thermolysis in dioxan, showed the process to be a *trans*-elimination with a large isotope effect. The ratio of the reaction rates for $[^2H_4]$-(**1d**) [$k(453.7\ K) = 1.3 \times 10^{-5}\ s^{-1}$] and $[^2H_0]$-(**1d**) [$k(453.7\ K) = 3.2 \times 10^{-5}\ s^{-1}$], was 1:2.5 {the isotope distribution in the sample of $[^2H_4]$-(**1d**) was $[^2H_4] = 95$, $[^2H_3] = 4$, $[^2H_2] = 1$, and $[^2H_1] = 0\%$}.

The deuterium distributions above were also supported by the ^{13}C n.m.r. spectra of (**7A**) and (**7B**), *i.e.* that of (**7B**) contained signals due to a mixture of *E*- and *Z*-3-deuterio-derivatives of (7) and $[^2H_0]$-(7) in a ratio of 1:1:1, while that of (**7A**) had signals due to a mixture of *E*-$[3\text{-}^2H_1]$- and *Z*-$[3\text{-}^2H_1]$-(7) and the 1-deuterio-derivative $[1\text{-}^2H_1]$-(7).§ Furthermore, the n.m.r. spectrum of the elimination product from $[^2H_4]$-(**1d**) contains peaks which are assigned exclusively to $[1,3,3\text{-}^2H_3]$cyclo-octene $[^2H_3]$-(**2d**).¶

To confirm the intramolecular nature of this *trans*-elimination reaction, we have measured the rates of the reaction of (**1d**) at various temperatures to obtain, in addition to $k(453.7\ K)$, $k(447.2\ K) = 1.6 \times 10^{-5}\ s^{-1}$, $k(441.2\ K) = 1.1 \times 10^{-5}\ s^{-1}$, $k(435.2\ K) = 6.3 \times 10^{-6}\ s^{-1}$, and $k(426.2\ K) = 2.6 \times 10^{-6}\ s^{-1}$, from which, we obtained $E_a = 33$ kcal mol^{-1} (1 cal = 4.184 J) and $\Delta S^\ddagger = -10$ cal K^{-1} mol^{-1} at 180.5 °C. The stereospecificity and kinetic features of the reaction together with its negative $\Delta S^\ddagger$ value,[4] indicate that it must be a concerted process, and, as a thermally allowed concerted process, the twelve-electron system should react in an *antara*-mode, which would be in accord with the observed *trans*-relationship; thus, the elimination may be designated as an $[{}_s8_\pi + {}_a2_\sigma + {}_s2_\sigma]$ process (route c, Scheme 2).**

In conclusion, the reverse selectivity of the dehydration of these alcohols from the usual acid-catalysed reaction should be of practical value, and the use of troponoids as reagents seems to provide a new selective method in organic synthesis.

Received, 23rd August 1982; Com. 958

References

1 H. Takeshita, H. Mametsuka, and K. Uchida, *Chem. Lett.*, 1982, 1071.

2 In general, cycloalkoxytropones can be prepared in good yields by the reaction between cycloalkanols, dicyclohexylcarbodi-imide, and tropolone, according to the method originally employed in phenyl ether preparations (*cf.*, E. Vowinkel, *Chem. Ber.*, 1966, **99**, 1479).

3 H. Takeshita, H. Mametsuka, and N. Matsuo, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 1137.

4 It is difficult to find a suitable reference on the kinetic data of this new reaction, but several kinetic measurements for the Cope rearrangement, a typical sigmatropic reaction, involving various types of reactants are known; all the $\Delta S^\ddagger$ values described in the following papers are in the range of -20 to -6 cal K^{-1} mol^{-1}; B. W. Bycroft and W. Landen, *Chem. Commun.*, 1970, 168; P. Metsner, T. N. Pham, and J. Vialle, *J. Chem. Res. (S)*, 1978, 478; M. J. S. Dewar and L. E. Wade, Jr., *J. Am. Chem. Soc.*, 1977, **99**, 4417.

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§ The n.m.r. spectrometric determination of the deuterio-derivatives of (7) was carried out in the gated decoupling mode (irradiation time = 2 s, pulse interval = 90 s); carbon signals were observed at δ 30.7 (t, *J* 19 Hz) and 31.7 (t, *J* 19 Hz) for *E*- or *Z*-$[3\text{-}^2H_1]$-(3) and at 61.1 (t, *J* 24 Hz) for $[1\text{-}^2H_1]$-(7) in a ratio of *ca.* 1:1:2.

¶ Predominant formation of $[1,3,3\text{-}^2H_3]$-(**2d**) has ruled out a possible involvement of a transannular hydrogen shift which often occurs in cyclo-octanes.

** In a sense, since tropolones are considered to be the tris-vinylogues of carboxylic acids, 2-alkoxytropones are vinylogues of the alkyl carboxylates. It is known that the latter give, when pyrolysed, olefins and carboxylic acids, *via* *cis*-elimination, *i.e.*, an $[{}_s2_\pi + {}_a2_\sigma + {}_s2_\sigma]$ process.