The Thermal Isomerization of Alkoxycycloheptatrienes and Some Reactions of Its Products[1]

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The tropylium ion (I), which is formed from 1, 3, 5-cycloheptatriene by a hydride abstraction, exhibits a highly electrophilic character and can thus readily give rise to compounds (general formula II) in which the cycloheptatriene group is bonded to an oxygen, sulfur, nitrogen, or carbon atom.[2] This cation, in aqueous solutions at a suitable pH, undergoes disproportionation to cycloheptatriene and tropone.[3] Ditropyl ether (III), which is easily obtained by the action of the base on I, also gives rise to cycloheptatriene and tropone in the presence of a trace of tropylium ion or an acid.[4] Thus, the above reactions would

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[1] A part of the Ph. D. Thesis of Kazuko Takahashi, Tohoku University (1963); partially presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1964.

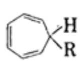
[2] For a review of tropylium ion, see a) W. von E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956); b) W. von. E. Doering, "Kekule Synposium" (1958); c) T. Nozoe, *Prog. Org. Chem.*, **5**, 132 (1961).

[3] Tropylium ion (I) exhibits a highly electrophilic character and can thus abstract a hydride from tropyl alcohol.

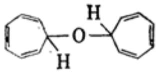
[4] a) T. Ikemi, T. Nozoe and H. Sugiyama, *Chem. Ind.*, **1960** 932; b) A. P. ter Borg, R. von Helden, A. F. Bickel, W. Renold and A. S. Dreiding, *Helv. Chim. Acta.*, **43**, 457 (1960); c) M. E. Volpin, Z. N. Parnes and D. N. Kursanov, *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, 950 (1960).

provide a very convenient route for the synthesis of troponoids and azulenoids, via the corresponding substituted tropones which should be obtainable from the corresponding tropylium ion (IV) formed from cycloheptatriene derivatives (II), by a similar hydride abstraction.[5] However, *O*-, *S*- and *N*-tropyl compounds are in general labile in acidic media,[2] and some *C*-tropyl compounds undergo fragmentation during treatment with strong acid.[2,6] For this reason, the direct formation of troponoids or azulenoids from cycloheptatriene derivatives is not generally feasible. In the presence of concentrated acids, alkoxycycloheptatrienes (alkyl tropyl ethers) (Va and Vb) and ditropyl ether (III) dissociate quantitatively to the cation (I). Furthermore, these are very effective tropylating reagents since they are quite soluble in most organic solvents and tend to react with phenols, tropolones, and compounds with an active methylene group, giving the corresponding cycloheptatriene derivatives.[7]


(I)



(II)



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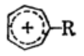
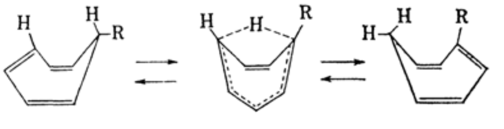


(IV)

During the last few years, the reactions of alkoxycycloheptatrienes and ditropyl ethers have been extensively investigated in our laboratory, with the aim of devising a synthesis of tropones and various derivatives of cycloheptatriene along the lines discussed above. In the course of this study, however, it was noticed that yields varied from time to time and that some reactions led to unexpected products. In order to clarify these ambiguities, we commenced extensive studies of the thermal reactions as well as of the effects of acids and alkalis on these alkoxycycloheptatrienes (Va and Vb).

Ethoxycycloheptatriene, on being mixed with phenols or tropolones, forms 7-substituted cycloheptatrienes, and, as has been previously noted, the heating of these products cases a migration of the double bonds.

The present authors obtained interesting results by following the thermal isomerization of alkoxycycloheptatrienes with the NMR technique. After we had started this work, a detailed study of the thermal isomerization of 7-substituted cycloheptatrienes was published by ter Borg et al.,[8] who examined changes in the NMR and mass spectra of 7-*D*-cycloheptatriene (II; R=D) at 100—140°C and in the NMR and ultraviolet spectra of 7-phenylcycloheptatriene (II; R=ph). They found that successive 1—5 transannular hydrogen shifts were taking place. From the kinetic study of this reaction, they concluded that the transition state had the symmetrical structure A shown below:



(A)

After the completion of our present study, Weth and Dreiding[9] published a short communication on the thermal isomerization of 7-methoxycycloheptatriene (Va); their results seem to be in substantial agreement with ours. The photoisomerization of Va and Vb in the vapor phase has also been noted by Chapman and Borden.[10]

In this paper we will report the results of a study of the thermal isomerization of

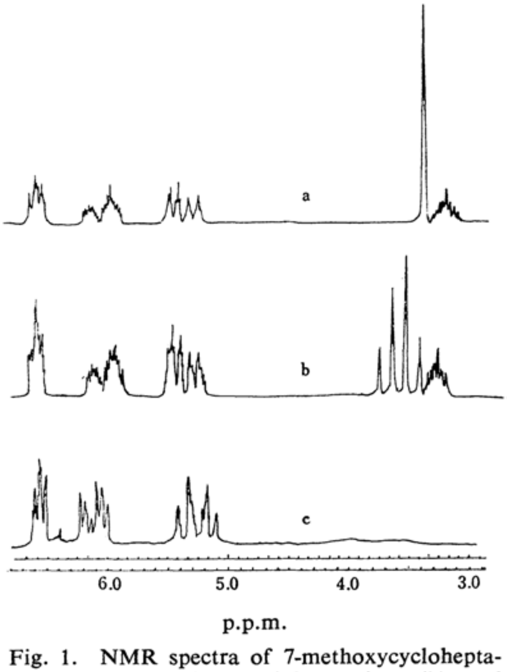


Fig. 1. NMR spectra of 7-methoxycycloheptatriene (a), 7-ethoxycycloheptatriene (b) and cycloheptatriene (c).

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[5] For reviews of troponoids and azulenoids, see T. Nozoe, "Non-Benzenoid Aromatic Compounds," Ed. by D. Ginsburg, Interscience, New York (1959); T. Nozoe, "Dai Yuki Kagaku" (Comprehensive Organic Chemistry), Vol. 13, Ed. by M. Kotake, Asakura shoten, Tokyo (1960), pp. 1—608.

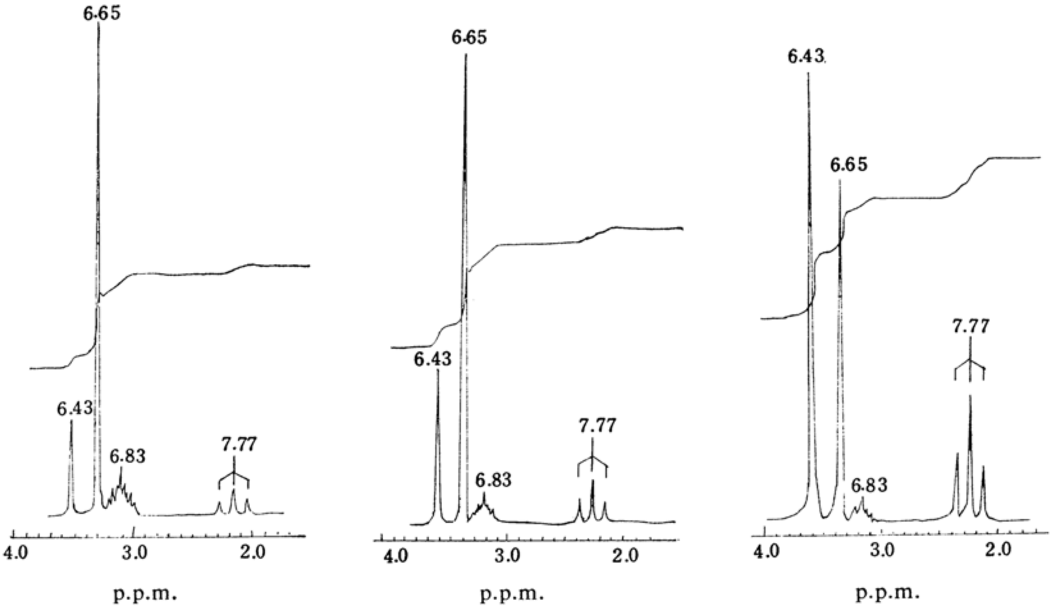
[6] K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959).

[7] a) T. Nozoe and K. Kitahara, *Chem. Ind.*, **1962**, 1192; b) T. Nozoe, K. Takahashi and H. Yamamoto, to be Published; c) T. Nozoe and T. Tezuka, to be published.

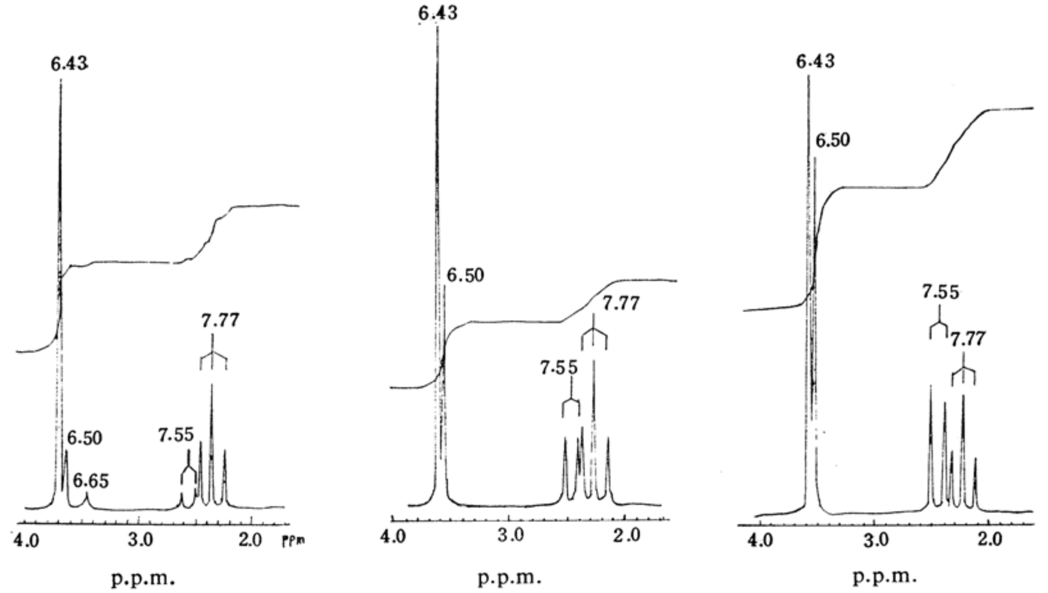
[8] a) A. P. ter Borg, H. Kloosterziel and N. van Meurs, *Rec. trav. chim.*, **82**, 717 (1963); b) A. P. ter Borg and H. Kloosterziel, ibid., **82**, 741 (1963); c) **82**, 1189 (1963).

[9] E. Weth and A. S. Dreiding, *Proc. Chem. Soc.*, **1964**, 59.

[10] O. L. Chapman and G. W. Borden, ibid., **1963**, 221.



a. for 17.67 hr. b. for 36.83 hr. c. foı 61.83 hr.



d. for 83.5 hr. e. for 149.3 hr. f. for 208.67 hr.

Fig. 2. NMR spectra of 7-methoxycycloheptatriene heated at 103° for various lengths of time.

methoxy- and ethoxy-cycloheptatriene; the reactions of the alkoxycycloheptatriene, obtained as the products of the above isomerization, will also be discussed.

7-Alkoxycycloheptatriene.—The 7-substituted cycloheptatrienyl structure can plausibly be assigned to the alkoxycycloheptatrienes (Va and Vb)[11] which are readily obtained by the addition of sodium hydrogen carbonate to a solution of tropylium ions in aqueous alcohols (see Fig. 1). As can be seen from Fig. 1a, the NMR spectrum of Va exhibits methyl signal at 6.65τ and a signal at 6.83τ resulting from the methine proton at the 7-position. By analogy with cycloheptatriene,[12] the signals

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[11] K. Conrow, *J. Am. Chem. Soc.*, **83**, 2347 (1961).

[12] a) G. Frankel, R. E. Carter, A. Mc Lachlan and J. H. Richards, ibid., **82**, 5846 (1960); b) R. Barton, L. Pratt and G. Wilkinson, ibid., **83**, 594 (1961).

at 4.46τ, 3.96τ and 3.59τ are assigned to the protons at the 1,6-, 2,5- and 3,4-positions respectively. Usually the protons at the 7-position of cycloheptatrienes appears as a triplet. However, this is not the case with 7-methoxycycloheptatriene and 7-ethoxycycloheptatriene (Fig. 1b), as these exhibit symmetrical multiplets, centered at 6.83τ and 6.76τ respectively, which are attributed to the existence of a long-range coupling between the 7-proton and the two protons β to it (H-2 and H-5), since the signals at 3.96τ and 3.97τ, due to the protons at positions 2 and 5 in methoxy- and ethoxy-cycloheptatriene, (Va and Vb), are more complicated than the corresponding signals in the spectrum of cycloheptatriene itself (Fig. 1c). The NMR spectrum of 7-ethoxycycloheptatriene (Vb) is quite similar to that of 7-methoxycycloheptatriene, except that in the former additional signals due to the ethyl group appear at 8.79τ and 6.43τ.

The Thermal Isomerization of Alkoxycycloheptatrienes.—The NMR spectrum of neat 7-methoxycycloheptatriene (Va), which had been heated for a short time in a sealed tube was measured in order to obtain information about the process of isomerization occurring in alkoxycycloheptatrienes heated in the 75—220°C temperature range. As an example, the NMR spectrum of a sapmle of 7-methoxycycloheptatriene which had been heated at 103°C for various lengths of time is shown in Fig. 2.

As can be clearly seen in Fig. 2, the signals at 6.65τ (methyl proton) and 6.83τ (H-7) decrease with time, and simultaneously two new signals, one a singlet at 6.43τ, 13.1 c./s. lower than the methyl signal of the starting material, and the other a triplet at 7.77τ (J=6.6 c./s.), gradually apppear (curve a) and increase in intensity. Continued heating causes the appearance of two new sets of signals, a singlet at 6.50τ and a doublet at 7.55τ (J=7.1 c./s.). These results are attributed to the occurrence of consecutive reactions, the second of which occurs after a period of 62 hr. at 103°C, 2.5 hr. at 120°C, or 1.5 hr. at 130°C (curve d). The signal at 6.65τ, due to Va, almost entirely disappears on prolonged heatings, e. g., 100 hr. at 150°C, and does not reappear again. It has, therefore, been concluded that the reverse reaction, VIa or VIb to Va or Vb, does not occur. The doublet signal at 7.55τ increases with time, and simultaneously the triplet signal at 7.77τ gradually decreases. At equilibrium new signals appear at 7.83τ (triplet; J=6.0 c./s.) and 6.58τ as a result of the corresponding methyl group (Fig. 3). It is now clear that the equilibrium mixture is characterized by the appearance of three signals, 6.43τ, 6.50τ and 6.58τ, in the ratio of 13.6 : 80.5 : 6.0. These signals, appearing on the heating of 7-methoxycycloheptatriene, are summarized in Table I.

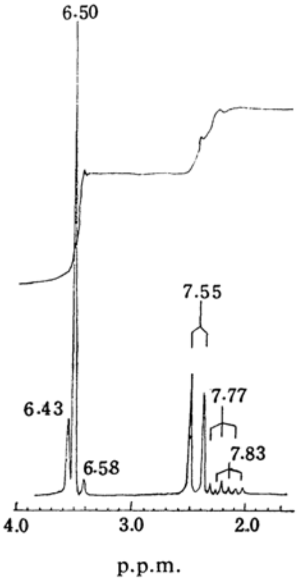


Fig. 3. NMR spectrum of 7-methoxycycloheptatriene which had been heated at 150°C for 100 hr.

Similar results were also obtained for 7-ethoxycycloheptatriene (Vb); these are shown in Table II. The signal due to the hydrogen at the 7-position is observed to undergo changes in the sequence of multiplet → triplet → doublet → triplet. The rate of isomerization seems to be of the same order as that for Va. The same sequence for the appearance of the signals is found at different temperatures for methoxy- and ethoxy-cycloheptatriene. This

TABLE I. THE CHANGES OCCURRING ON HEATING OF 7-METHOXYCYCLOHEPTATRIENE

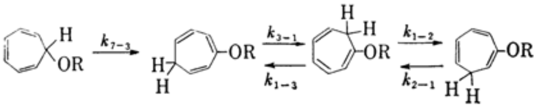
The sequence of the appearance of the signals	The type of signals	Chemical shift of H-7 τ	Coupling constant c./s.	Chemical shift of CH_3 τ	Substituted position of OCH_3
1	Multiplet	6.83	ca. 4.2	6.65	7
2	Triplet	7.77	6.6	6.43	3
3	Doublet	7.55	7.1	6.50	1
4	Triplet	7.83	6.0	6.58	2

TABLE II. THE CHANGES OCCURRING ON HEATING OF 7-ETHOXYCYCLOHEPTATRIENE

The sequence for the appearance of the signals	The type of signals	Chemical shit of H-7, τ	Coupling constant c./s.	Substituted position of OEt
1	Multiplet	6.76	ca. 4.2	7
2	Triplet	7.79	6.8	3
3	Doublet	7.54	7.2	1
4	Triplet	7.87	6.6	2

means that successive migrations of hydrogen are taking place and that the same 1—5 transannular hydrogen shift observed by ter Borg et al.[8] for 7-*D*- and 7-phenyl-cycloheptatriene is operating in the case of alkoxycycloheptatrienes. As is shown in Tables I and II, all these chemical shifts can be assigned to the revelant isomer from which they originate.

Kinetic Study.—The ultraviolet spectrum of 7-methoxycycloheptatriene (Va) exhibits an absorption maximum at 255 mμ (log ε=3.61), and the ultraviolet spectrum of 3-methoxycycloheptatriene (VIa) shows a peaks at 261 mμ (log ε=3.60). Therefore, the ultraviolet spectrophotometric method could not conveniently be applied to a study of the rate of



Va : R=Me VIa : R=Me VIIa : R=Me VIIIa : R=Me
Vb : R=Et VIb : R=Et VIIb : R=Et VIIIb : R=Et

thermal isomerization, Va → VIa, as was done in the case of phenylcycloheptatriene. As was mentioned in the preceding section, methyl signals appear at different fields, e.g., at 6.65τ for Va and 6.43τ for VIa. The area of these two signals can be separately measured by NMR an integrator technique thus provides a useful method for studying the kinetics.

In Fig. 4, a plot of the area proportion to the total area against time is made for each methyl signal. The straight line indicates that

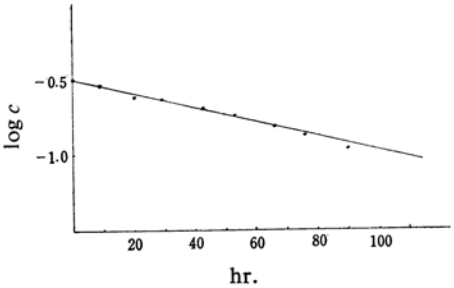


Fig. 4. The logarithm of area of methyl signal proportional to total area (log c) as a function of time at 99.0°C.

TABLE III. RATE CONSTANTS OF ISOMERIZATION OF 7-METHOXYCYCLOHEPTATRIENE

Temp., °C	K_{7-3}
116.3	1.76×10^{-5}
99.0	3.04×10^{-6}
76.1	3.36×10^{-7}

the isomerization of Va to VIa is of the first order and that the rate constant, k_{7-3}, for the conversion of 7-methoxycycloheptatriene (Va) to the first isomer 3-methoxycycloheptatriene (VIa) can be obtained from the slope of the line. This rate constant at different temperatures is given in Table III. These figures were derived from the NMR spectra of aliquots taken at special time intervals. However, it was found necessary to purify the aliquots by vacuum distillation in order to remove a small amount of a high boiling product before measuring the spectra. The yield of a high boiling product became progressively larger as the heating period and temperature were increased, but it did not go beyond 10% under the conditions used.

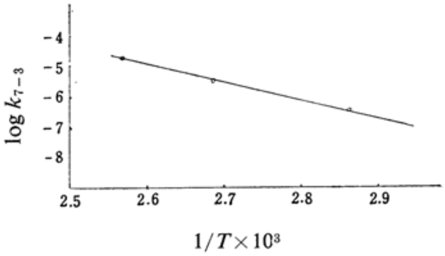


Fig. 5. Rate constants of the hydrogen shifts as a function of temperature.

In Fig. 5, a linear relationship between log k_{7-3} and $1/T$ is demonstrated. By the method of least squares, Eq. 1 was obtained for the straight line in Fig. 5:

$$\log k_{7-3} = 10.04 - 5.774\times10^3\,T^{-1} \qquad (1)$$

From this relationship, log A and the experimental activation energy, ΔE, are found to be 10.04 and 26.407 kcal. mol^{-1} respectively. Thus, from the absolute rate theory, the following figures are calculated by assuming the transmission coefficient to be unity: enthalpy

TABLE IV. RATE CONSTANTS OF THE ISOMERIZATION OF CYCLOHEPTATRIENE AND 7-METHOXYCYCLOHEPTATRIENE

Temp. °C	Cycloheptatriene	7-Methoxycycloheptatriene
98	3.8×10^{-8}	3.07×10^{-6}
121	6.0×10^{-7}	2.48×10^{-5}
140	3.2×10^{-6}	1.17×10^{-4}

TABLE V. RATE CONSTANTS OF THE ISOMERIZATION OF 7-PHENYLCYCLOHEPTATRIENE AND 7-METHOXYCYCLOHEPTATRIENE

Temp. °C	7-Phenylcycloheptatriene	7-Methoxycycloheptatriene
80.4	6.83×10^{-7}	5.15×10^{-7}
99.9	4.76×10^{-6}	3.68×10^{-6}
120.2	3.60×10^{-5}	2.31×10^{-5}

of activation: $\Delta H^{\neq}=25.7$ kcal. mol^{-1} and entropy of activation: $\Delta S^{\neq}=-15.0$ cal. mol$^{-1}\cdot$deg^{-1}.

For comparison, Tables IV and V list values of the rate constant, k_{7-3}, at different temperatures for the thermal isomerization of cycloheptatriene itself, for that of 7-phenylcycloheptatriene to 3-phenylcycloheptatriene, and for 7-methoxycycloheptatriene, the values for the last compound being calculated from Eq. 1. 7-Methoxycycloheptatriene is seen to undergo isomerization about 100 times faster than cycloheptatriene; k_{7-3} is almost identical in the cases of phenylcycloheptatriene and of methoxycycloheptatriene.

Although a quantitative analysis could not be made of ethoxycycloheptatriene, it seems that its rate of isomerization is not markedly different from that of methoxycycloheptatriene at the initial stage. However, the NMR spectra of the pyrolysates obtained by heating 7-methoxycycloheptatriene and 7-ethoxycycloheptatriene at 195°C for 2 hr., indicate that the former consists of a mixture of 3-methoxy-, 1-methoxy- and 2-methoxy-cycloheptatriene in a ratio of 18.5, 77.0, and 4.63, whereas the latter contains only 3-ethoxy-, and 1-ethoxy-cycloheptatriene in a ratio of 15.2 and 84.8. It is interesting to note that the formation of 2-ethoxycycloheptatriene is not detected in the isomerization of 7-ethoxycycloheptatriene. This may imply that there is some difference in the ratio of k_{2-1} to k_{1-2} for methoxy- and ethoxy-cycloheptatriene.

The negative sign of $\Delta S^{\neq}$ indicates that this reaction may proceed through a transition state such as that shown by A. The value, -15.0 cal. mol^{-1} deg^{-1}, seems to be reasonable when compared with the corresponding value, -8.2 cal. mol^{-1} deg^{-1}, for cycloheptatriene. The fact that this value (-15.0 cal. mol^{-1} deg^{-1}) is even lower than that (-11.7 cal. mol^{-1} deg^{-1}) for phenylcycloheptatriene may be ascribed to some contribution of the lone pair of electrons to the rigidity of the transition state. However, before drawing any final conclusion it is necessary to carry out further investigations.

Chemical Reactions of Alkoxycycloheptatrienes. — As has been seen above, a simple method is now available for the preparation of cycloheptatriene derivatives in which the alkoxy group is present at positions other than the 7-position. This makes it possible to compare the 7-alkoxycycloheptatrienes with their isomers with regard to their reactivity towards acids, alkalis and dehydrogenating reagents.

When a 7-alkoxycycloheptatriene was shaken with a 6 N hydrochloric acid, tropylium ion (I) was formed in a quantitative yield. The similar treatment of a 7-alkoxycycloheptatriene with a dilute aqueous hydrogen chloride solution at pH 2 for 30 min. gave rise to a 65% yield of the cation I as well as to the formation of some tropone and cycloheptatriene by a disproportionation; however, no traces of the starting material, Va and Vb, were recovered. When a 10% aqueous solution of tropylium bromide (pH=2) was shaken, tropone was slowly formed; this is attributed to a disproportionation of the tropylium ions and tropylalcohol.

On the other hand, the treatment of a mixture of a 3-alkoxycycloheptatriene (VIa and VIb) and a 1-alkoxycycloheptatriene (VIIa and VIIb) with 6 N hydrochloric acid did not result in the formation of tropylium ions to any detectable extent. Similarly, a 95% recovery of the starting materials (as determined by NMR spectral analysis) was obtained when 3-ethoxycycloheptatriene (VIb) and 1-ethoxycycloheptatriene (VIIb) were shaken for 30 min. with 1 N hydrochloric acid at 0°C. When 0.5 N hydrochloric acid was used, 98% of the starting materials was again recovered. These experiments show that, in contrast to 7-alkoxycycloheptatrienes, the isomerization products, 1- and 3-alkoxycycloheptatrienes, are stable in dilute aqueous acid.

When 7-methoxycycloheptatriene was heated at 103°C for 55—60 hr. and when the reaction was then stopped at a point before the doublet signal due to 1-methoxycycloheptatriene (VIIa) appeared in the NMR spectrum, a mixture of Va and VIa was obtained. If this mixture was then shaken with cold 0.5 N hydrochloric acid, Va was transferred to the aqueous phase as tropylium ions, it was thus possible to isolate pure 3-methoxycycloheptatriene (VIa). Pure 3-ethoxycycloheptatriene (VIb) could be obtained by a similar procedure. Fractional distillation could also be used to separate a mixture of 7-ethoxycycloheptatriene (b. p. 71—76°C/20 mmHg) and 3-ethoxycycloheptatriene (81—82°C/20 mmHg). The NMR spectra of 3-methoxycycloheptatriene and 3-ethoxycycloheptatriene are shown in Figs. 6 and 7.

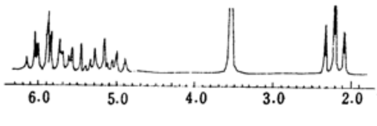


Fig. 6. NMR spectrum of 3-methoxycycloheptatriene and some reaction of its products.

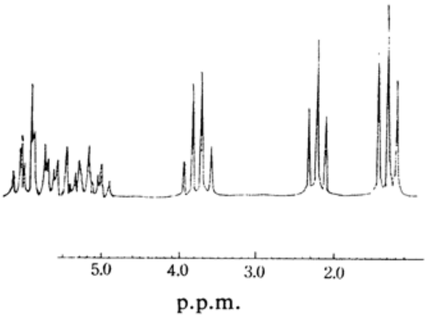
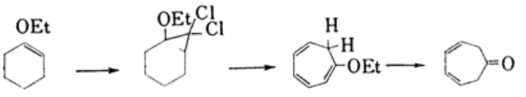


Fig. 7. NMR spectrum of 3-ethoxycycloheptatriene.

Parham et al.[13] have reported that 1-ethoxycycloheptatriene (VIIb) was obtained by heating 1-ethoxy-7, 7-dichlorocarane (X) in quinoline, the X having been prepared from 1-ethoxycyclohexene (IX) and dichlorocarbene.



(IX) (X) (VIIb) (XI)

Parham et al. have also obtained a good yield (95%) of 2, 7-dihydrotropone (XI)[14] through the action of a small amount of acid on a methanol solution of 1-ethoxycycloheptatriene. When 7-ethoxycycloheptatriene was kept at 195°C for 2 hr., it afforded a mixture of 84.8% 1-ethoxycycloheptatriene (VIIb) and 15.19% 3-ethoxycycloheptatriene (VIb), which, after hydrolysis and purification by distillation, afforded a liquid in a 69% yield. The NMR spectrum (see Fig. 8) of this liquid shows a sharp doublet at 7.01τ ($J=5.7$ c./s.) and the presence of vinylic protons and ethylenic protons whose signals have intensities in the ratio of 1 : 1, strongly indicating that the liquid may be 2, 7-dihydrotropone (XI). Since no signals are observed above 7.01τ, the formation of 2, 5-dihydrotropone could not be confirmed.

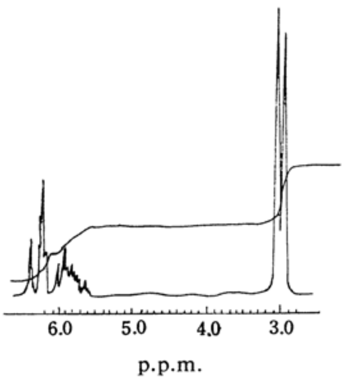


Fig. 8. NMR spectrum of 2, 7-dihydrotropone.

As has already been noted, the isomerization products, VIa and VIb, VIIa and VIIb, and VIIIa and VIIIb, are stable in dilute aqueous acid. However, the treatment of them with 6 N hydrochloric acid gave cycloheptadienone (XI or its isomer) and also XII as a liquid, b. p. 40—45°C/7 mmHg, and its dimer (XIII) (b. p. 115°C/1 mmHg). The former XII is considered to be hydroxycycloheptenone and the latter XIII, a dimer of XII on the basis of the elementary analyses of their 2, 4-dinitrophenylhydrazones. However, the structure of the latter is not clear.

7-Alkoxycycloheptatriene was found to be stable in alkali at room temperature.

The reaction of 7-alkoxycycloheptatriene with such dehydrogenating reagents as phosphorus pentachloride (Volpin's method[15]) does not give rise to a dehydrogenated product but instead, forms tropylium ions through the elimination of the alkoxy group. However, the treatment of a mixture of 1- and 3-alkoxycycloheptatriene in carbon tetrachloride with 2 molar equivalents of phosphorus pentachloride does not yield tropylium ions but instead produces an alkoxytropylium ions (IV: R= OMe or OEt) in more than a 50% yield. Alkoxytropylium ions separated as a double salt with phosphorous pentachloride from carbon tetrachloride; when this salt was treated with chloroplatinic acid in acetonitrile, the chloroplatinate of IV (R=OMe or OEt) was precipitated as prisms. When the aqueous solution of the double salt was heated, tropone was formed in a quantitative yield.

An unsuccessful attempt was made to prepare

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[13] W. E. Parham, R. W. Soeder and R. M. Dodson, *J. Am. Chem. Soc.*, **84**, 1756 (1962).

[14] J. Meinwald, S. L. Emerman, N. C. Yang and G. Buchi, ibid., **77**, 4401 (1955).

[15] a) D. N. Kursanov and M. E. Volpin, *Doklady Akad. Nauk S. S. S. R.*, **113**, 339 (1957); b) M. E. Volpin, I. S. Akhrem and D. N. Kursanov, *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, **1957**, 760.

ethoxytropopylium bromide by allowing a mixture of 1- and 3-ethoxycycloheptatriene in carbon tetrachloride to react with bromine, and then attempting a dehydrobromination under reduced pressure; however, tropone was obtained. This may be explained by assuming that alkoxytropoylium bromide, a reaction intermediate, was hydrolyzed to tropone during the reaction.

It was hoped that the oxidation of a 3-alkoxycycloheptatriene would yield a 4-alkoxytropone. However, when 3-ethoxycycloheptatriene in dry dioxane was oxidized with selenium dioxide, it unexpectively gave only tropone. Although doubt still remains, this may be attributed to the fact that 3-alkoxycycloheptatrienes (VI) are initially oxidized to an alkoxytropylium salt (IV), which subsequently hydrolyzed to tropone.

The present study has made it clear that 7-alkoxycycloheptatrienes can be converted to alkoxytropylium ions by dehydrogenation after the thermal isomerization. It is also apparent that tropones can be obtained from the dihydrotropones (XI) which are the hydrolysis products of the above isomers of 7-alkoxycycloheptatrienes.

The 7-alkoxycycloheptatrienes gave cation I by the action of acid, and they also reacted with compounds with active hydrogens or with nucleophilic substances,(7) the presence of a trace of acid being sometime necessary. It has thus been established that 7-alkoxycycloheptatrienes may be used effectively as tropylating reagents. As has been mentioned above, one of the advantages of the alkoxycycloheptatrienes (Va and Vb) is that they are readily soluble in organic solvents. In contrast to cation I, alkoxycycloheptatrienes alone do not show any dehydrogenating or oxidizing character. We have also studied the thermal isomerization of alkylmercapto- and amino-cycloheptatrienes, the results of which study will be shortly reported in this Bulletin.

Experimental

Reaction Rate Measurements. — Alkoxycycloheptatrienes (Va and Vb) were sealed in tubes (8 mm. in outer diameter and 40 mm. long) and hung in the vapor of refluxing carbon tetrachloride (76.1°C), water (99.0°C) and acetic acid (116.3°C) respectively. The temperature was uniform over the whole length of the tubes. At regular intervals the tube was taken out and the contents were separated by distillation into alkoxycycloheptatriene and a high boiling product. The NMR spectrum (60 Mc./s.: A-60 Varian spectrometer) was recorded and electrically integrated.

The high-boiling product was found to form more readily from methoxycycloheptatriene than from ethoxycycloheptatriene. When 7-methoxycycloheptatriene (Va) and 7-ethoxycycloheptatriene (Vb) were kept under the same conditions, at 195°C for 2 hr. (these conditions were far more drastic than those applied to the determination of the rate constant k_{7-3}), Vb gave a high boiling product in 13.35%, whereas Va gave it in 18.15%.

7-Ethoxycycloheptatriene (Vb).—7-Ethoxycycloheptatriene was prepared by a slight modification of the method described by Conrow.(11) A mixture of 6 l. of dry carbon tetrachloride and 1 kg. of phosphorus pentachloride was shaken for 30 min., and then 320 g. of cycloheptatriene was added. The reaction mixture was shaken for 5—6 hr. and allowed to stand overnight. The separated precipitates were collected and poured into 2.6 kg. of ice. After the addition of 260 ml. of ethanol, the solution was neutralized by sodium hydrogencarbonate and extracted by ether (or benzene). The extract was dried over sodium carbonate, and the solvent was evaporated. The residue was then distilled under reduced pressure, giving 173 g. of a colorless liquid, 7-ethoxycycloheptatriene, b. p. 72—73°C/25 mmHg.

The Action of 6 N Hydrochloric Acid on 7-Alkoxycycloheptatrienes (Va and Vb).—A mixture of 300 mg. of Vb and 1 ml. of 6 N hydrochloric acid was shaken for 0.5 hr. To the resulting mixture a 30% aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ was added, giving 596 mg. (90.6%) of pale yellow crystals. Its infrared spectrum was identical with that of tropylium chloroplatinate.

Under identical conditions but starting from 300 mg. of Va, 644 mg. (89%) of tropylium chloroplatinate was obtained.

The Action of 1 N Hydrochloric Acid on 7-Methoxycycloheptatriene (Va).—A mixture of 3 g. (0.025 mol.) of Va and 23.58 ml. of 1 N hydrochloric acid was adjusted to pH 2 by the addition of some water and shaken for 5 hr. at room temperature. The reaction mixture was then extracted with chloroform. The extract was dried over sodium sulfate, and the solvent was evaporated to give 666 mg. of a liquid. Infrared and ultraviolet spectral analyses showed that the liquid contained 408 mg. (theoretical yield; 31.4%) of tropone. The aqueous layer was saturated with sodium perchlorate to separate 3.03 g. (64.8%) of colorless needles, the infrared spectrum of which was identical with that of tropylium perchlorate.

The Action of Water on Tropylium Bromide.—Tropylium bromide (2.205 g.) was dissolved in about 20 ml. of water, and the pH of the solution was adjusted to ca. 2. by the addition of water. This solution was then shaken vigorously for 5 hr. at room temperature. The reaction mixture was allowed to stand overnight and was extracted with chloroform. After it had dried over sodium sulfate, the solvent was evaporated, giving 212 mg. of a liquid. Ultraviolet spectral analysis showed that the liquid contained 145.5 mg. (theoretical yield; 21.2%) of tropone. The aqueous layer was saturated with sodium perchlorate to separate 1.92 g. (78.8%) of tropylium perchlorate.

The Action of 6 N Hydrochloric Acid on Thermally-Isomerized Methoxycycloheptatriene.—7-Methoxycycloheptatriene (Va) was heated for 2 hr. at 195°C and distilled to remove the high boiling product. The distillate was a mixture of 3-methoxycycloheptatriene (VIa), 1-methoxycycloheptatriene (VIIa) and 2-methoxycycloheptatriene (VIIIa) in the ratio of 18.5 : 7.70 : 4.63, judging from the analysis of MNR spectrum. The above-obtained mixture (400 mg.) and 1 ml. of 6 N hydrochloric acid were shaken for 30 min. When the reaction mixture was extracted with chloroform, 263 mg. of a brown liquid was afforded by the evaporation of the solvent. Infrared spectrum of the liquid was virtually identical with that of a mixture of XII and the XIII dimer. From the aqueous layer, no precipitates appeared upon the addition of a 30% aqueous solution of $H_2PtCl_6 \cdot 6H_2O$.

The Action of 1 N Hydrochloric Acid on Thermally-Isomerized Ethoxycycloheptatriene. — When 7-ethoxycycloheptatriene was heated for 2 hr. at 195°C, it gave a liquid which contained 3-ethoxycycloheptatriene (VIb) and 1-ethoxycycloheptatriene (VIIb) in the ratio of 15.19 : 84.8. To 4 g. of this liquid, 33 ml. (1.1 mol. eq.) of 1 N hydrochloric acid was added. After it had been shaken for 30 min. at 0°C, the reaction mixture was extracted with chloroform. The extract was dried over sodium sulfate, and the solvent was evaporated in vacuo, affording a yellow liquid. Its NMR spectrum showed that this liquid contained 3.87 g. (96.7%) of the starting material.

The Action of 0.5 N Hydrochloric Acid on Thermally-Isomerized Ethoxycycloheptatriene.—To 4 g. of the thermally-isomerized ethoxycycloheptatriene, which comprises 15.19% of VIb and 84.8% of VIIb, 66 ml. of 0.5 N hydrochloric acid was added. When this mixture was treated in the same manner as described above, it afforded 3.90 g. (97.5%) of the starting material.

3-Methoxycycloheptatriene (VIa). — 7-Methoxycycloheptatriene (Va) was heated for 55—60 hr. at 106°C, affording a liquid which was found to be a mixture of 40% of Va and 60% of VIa by a comparison of its NMR spectrum with those of Va and VIa. To 300 ml. of 0.5 N hydrochloric acid, 34.8 g. of this mixture was added at 0°C. This mixed solution was shaken for 30 min. at 0—5°C and then extracted with chloroform. The extract was washed with a saturated aqueous solution of sodium hydrogen carbonate and dried over sodium sulfate. After the evaporation of the solvent, the residue was distilled under reduced pressure to give 17.10 g. of 3-methoxycycloheptatriene (VIa), b. p. 74—75°C/15 mmHg, 716 mg. of substance A b. p. 60—100°C/0.5 mmHg, and 527 mg. of B b. p. 100—125°C/0.5 mmHg. The NMR spectra showed A to be a mixture of VIa and B, and B to be a mixture of XII and XIII. An undistilled residue (6.76 g.) remained.

3-Ethoxycycloheptatriene (VIb).—a) Under the same conditions as with 3-methoxycycloheptatriene, 34.0 g. of a mixture of Vb and VIb afforded 20.29 g. of 3-ethoxycycloheptatriene, b. p. 76 — 80°C/15 mmHg and 294 mg. of a yellow oil, b. p. 125—130°C/0.5 mmHg. The NMR spectrum of the latter is identical with that of above B. An undistilled residue (2.77 g.) remained.

b) After 19 g. of 7-ethoxycycloheptatriene had been heated for 2.5 hr. at 130°C, the thermally-isomerized product was distilled fractionally through a column which was 25 mm. in diameter and 30 cm. long. A colorless liquid, 9.24 g. of A, b. p. 71—76°C/20 mmHg, 3.08 g. of B, b. p. 76—81°C/20 mmHg, and 2.71 g. of C, b. p. 81—82°C/20 mmHg were obtained. From the NMR spectral comparison, it was clarified that A and C were identical with Vb and VIb respectively, and that B was a mixture of the two. An undistilled residue (3.20 g.) remained.

2, 7-Dihydrotropone (XI). — 7-Ethoxycycloheptatriene was heated for 2 hr. at 195°C and distilled under reduced pressure to give a liquid which contained 84.8% of VIIb and 15.19% of VIb. A mixture of 80 ml. of methanol, 11 ml. of water and 10 ml. of concentrated hydrochloric acid was then added. After this mixture had been stirred for 2 hr. at 15—20°C, cold water was added to dilute the reaction mixture to a volume of 200 ml. The resulting solution was extracted with 100 ml. of chloroform. After the extract had been washed with a saturated aqueous solution of sodium hydrogen carbonate, the solvent was evaporated to give 4.25 g. of a liquid. By the vacuum distillation of the liquid, 3.28 g. (68.87%) of XI, b. p. 71—74°C/20 mmHg was obtained.

The Action of 6 N Hydrochloric Acid on Thermally-Isomerized Ethoxycycloheptatriene. — 7-Ethoxycycloheptatriene (Vb) was heated for 1 hr. at 200°C and distilled to afford a clear liquid which was more than 80% 1-ethoxycycloheptatriene (VIIb). A mixture of 15 g. of this liquid and 51 ml. of 6 N hydrochloric acid was shaken vigorously at room temperature for 5 hr. The reaction mixture was then extracted with 100 ml. of chloroform, and the extract was washed with a saturated aqueous solution of sodium hydrogen carbonate. After the evaporation of the solvent, 13.09 g. of a brown oil was obtained; 4 g. of it was distilled in vacuo to give 314 mg. of a colorless liquid (XII), b. p. 40—55°C/7 mmHg and 1.86 g. of a pale yellow oil (XIII), b. p. 115°C/1 mmHg.

2, 4-Dinitrophenylhydrazone of XII.—A mixture of 180 mg. of XII, 10 ml. of ethanol and 825 mg. of 2, 4-dinitrophenylhydrazine was refluxed for 1 hr.; then the excess 2, 4-dinitrophenylhydrazine was removed by hot filtration. The filtrate was cooled in ice and the resulting crystals recrystallized from ethanol to give red plates, m. p. 175—181°C.

Found: C, 51.67; H, 4.42; N, 17.96. Calcd. for $C_{13}H_{14}O_5N_4$: C, 50.98; H, 4.61; N, 18.29%.

2, 4-Dinitrophenylhydrazone of XIII.—A mixture of 300 mg. of XIII, 10 ml. of ethanol and 800 mg. of 2, 4-dinitrophenylhydrazine was refluxed for 1 hr.; then the resulting crystals were fractionally recrystallized from ethanol, giving red crystals from the easily soluble part and yellow crystals from the sparingly soluble part. Although the former was difficult to purify, the latter was purified by repeated recrystallization, giving yellow needles, m. p. 161—162°C.

Found: C, 60.64; H, 4.99; N, 13.70. Calcd. for $C_{20}H_{20}O_5N_4$: C, 60.60; H, 5.09; N, 14.14%.

The Action of Phosphorus Pentachloride on Alkoxycycloheptatriene (Va and Vb).—A mixture of 3.98 g. (2.6 mol. eq.) of phosphorus pentachloride and 35 ml. of anhydrous carbon tetrachloride was stirred for 30 min., and then a solution of 1 g. of Vb in 1 ml. of carbon tetrachloride was stirred in. Immediately colorless precipitates were separated out. Stirring was then continued for a further 5 hr. at 15—20°C. The reaction mixture was allowed to stand overnight and poured onto 5 g. of ice. Sodium perchlorate was added to the aqueous layer, giving 1.13 g. (81%) of tropylium perchlorate. Under identical conditions but starting with 1 g. of Va, 1.34 g. (85.8%) of tropylium perchlorate was obtained.

Methoxytropylium Ions (IV; R=OMe).—To a mixture of 2.15 g. (2 mol. eq.) of phosphorus pentachloride and 30 ml. of anhydrous carbon tetrachloride, a solution of 1 g. of thermally-isomerized methoxycycloheptatriene (a mixture of 18.5% of VIa, 77.0% of VIIa, and 4.63% of VIIIa) in 1 ml. of carbon tetrachloride was added. After 6 hr. stirring, the reaction mixture was allowed to stand overnight. The resulting colorless precipitates were separated by filtration under dry air; after the precipitates had been dried under the vacuo, they were poured into 2 ml. of anhydrous acetonitrile. The resulting solution was filtered to remove insoluble substances, and then to the filtrate was added, drop by drop, a 30% solution of $H_2PtCl_6\cdot 6H_2O$ in acetonitrile to give 152 mg. yellow prisms, m. p. 180°C (decomp.)

Found: C, 29.52; H, 2.78; Pt, 29.79. Calcd. for $C_8H_9O_{1/2}PtCl_6$: C, 29.55; H, 2.79; Pt, 30.01%.

The filtrate was then concentrated, giving further 531 mg. of crystals (Total yield: 683 mg.). An infrared spectrum of the crystals differs from that of the chloroplatinate of tropone.

Ethoxytropylium Ions (IV; R=OEt).—Under the same conditions with methoxytropylium ions, 600 mg. of thermally-isomerized ethoxycycloheptatriene (a mixture of 15.19% of VIb and 84.81% of VIIb) gave 669 mg. of pale orange prisms, m. p. 164—165°C (decomp.).

Found: C, 32.15; H, 3.25; Pt, 28.55. Calcd. for $C_{18}H_{22}O_2PtCl_6$: C, 31.89; H, 3.27; Pt, 28.76%.

When absolute alcohol was used instead of anhydrous acetonitrile, 1 g. of thermally-isomerized ethoxycycloheptatriene also gave 194 mg. of chloroplatinate of IV; R=EtO.

The Action of Bromine on Thermally-Isomerized Ethoxycycloheptatriene.—To a cold solution of 4 g. of thermally-isomerized ethoxycycloheptatriene (a mixture of 15% of VIb and 85% of VIIb) in 35 ml. of carbon tetrachloride, a solution of 4.7 g. of bromine in 13 ml. of carbon tetrachloride was stirred in drop by drop. Stirring was then continued for a further 5 hr. at 15°C, after which the solvent was evaporated at 40—50°C under reduced pressure. The residue was allowed to stand for 3 days at 50°C under 100 mmHg. At the end of this period, 4.68 g. of strongly hydroscopic black precipitates were obtained. These precipitates (1.42 g.) were added to 2 ml. of acetonitrile, and the insoluble substance was removed by filtration. A solution of $H_2PtCl_6\cdot 6H_2O$ (1 g.) in 2 ml. of acetonitrile was added to the filtrate, giving 139 mg. of orange needles. Their infrared spectrum was identical with that of the chloroplatinate of tropone.

Tropone from Ethoxytropylium Ions.—Starting from 3 g. of thermally-isomerized ethoxycycloheptatriene, 11.24 g. of phosphorus pentachloride and 120 ml. of carbon tetrachloride, ethoxytropylium ions were obtained as 7.02 g. of double salt with phosphorus pentachloride. This salt was dissolved in water, and the solution was warmed on a water bath and neutralized by the addition of sodium hydrogen carbonate. The reaction product was extracted with chloroform, giving 1.23 g. of an oil. Its infrared spectrum was identical with that of tropone, and by the action of picric acid, this oil afforded 3.5 g. of topone picrate.

The Action of Selenium Oxide on 3-Ethoxycycloheptatriene (VIb).—Into a solution of 5 g. of VIb in 100 ml. of dry dioxane, 8.15 g. (2 mol. eq.) of selenium oxide under a nitrogen atmosphere was stirred. The mixture was heated at 120—125°C for 3 hr. under stirring and allowed to stand overnight. The selenium with separated was removed by filtration, and the solvent was evaporated under reduced pressure. Ether was added to the residue, and 2.15 g. of an oil was obtained by the evaporation of the solvent. Its infrared spectrum was identical with that of tropone, and by the action of hydrazine hydrate, the oil afforded 1.59 g. of 2-aminotropone.[16]

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