were very closely similar. It was concluded that the identity or non-identity of quercitol *diastereomers* cannot be established reliably by routine infrared measurements with instruments of limited resolving power. This is in contrast to the n.m.r. measurements, which gave spectra that differed markedly for the two diastereomers.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES, LOS ANGELES 24, CALIF.]

Isomerization of Alkyl Tropilidenes[1]

BY KENNETH CONROW[1a]

RECEIVED DECEMBER 20, 1960

The monomethyltropilidenes are involved in reversible hydride exchange equilibria with tropylium and methyltropylium ions in acetonitrile solvent. The composition of the equilibrium mixture of the methyltropilidene isomers and the equilibrium constant for hydride exchange between the equilibrium mixture of methyltropilidenes and tropylium ion have been measured. From these results, it follows that the methyltropylium ion is 3.7 ± 0.4 kcal./mole more stable than the unsubstituted tropylium ion. Crude measures of the rate of hydride transfer from 7-methyltropilidene to tropylium ion ($k_2 \sim 1.8 \times 10^{-3}$) and to methyltropylium ion ($k_2 \sim 3 \times 10^{-4}$) also were obtained. No evidence was observed for isomerization in solution by mechanisms other than that of hydride exchange.

The reaction mixtures involved in the study of electrophilic fragmentation of 7-(functionally substituted alkyl)-tropilidenes[2] invariably contain an electrophile, a 7-alkyltropilidene and tropylium ion. The possibility that the electrophile or the tropylium ion might isomerize the 7-alkyltropilidene to 1-, 2- or 3-alkyltropilidenes (which cannot fragment except by isomerization back to the 7-isomer) in a reaction competitive with the fragmentation reaction prompted a study of the isomerization of 7-alkyltropilidenes. To avoid the complication which would arise from a competing fragmentation reaction, simple 7-methyl- and 7-ethyltropilidenes were selected for this study.

Attention first was turned to seeking a way to identify the various alkyltropilidenes when and if isolated in a pure state. Since pyrolysis of tropilidene itself gives rise to toluene[3] it was expected that alkyltropilidenes would give α-, *o*-, *m*- and *p*-alkyltoluenes. On the basis of Woods'[3] suggested mechanism, 7-alkyltropilidene would give α-alkyltoluene, 1-alkyltropilidene would give α- and *o*-, 2-alkyltropilidene would give *o*- and *m*- and so on. However, it was found that pyrolysis of 7-ethyltropilidene at 400° gave a mixture of 1-, 2-, 3- and 7-ethyltropilidene with little, if any, ring contraction to toluene derivatives. Since isomerization of ethyltropilidene occurs at this temperature prior to ring contraction, any mixture of alkylbenzenes which might be obtained at higher temperature will be that derived from some isomeric mixture of ethyltropilidenes regardless of which isomer was utilized in the pyrolysis. This result eliminates the possibility of using pyrolysis as a means of identification of structure.

The production of tropylium ion by various mild oxidizing agents[4] suggests that any oxidation to substituted benzaldehydes or benzoic acids observed with stronger oxidizing agents[5] would proceed through tropylium ion as an intermediate. In this event, all of the isomeric alkyltropilidenes would proceed through a common intermediate aud no information about isomerization in the alkyltropilidene could be gained by such an oxidative process.

Processes based on the Diels–Alder reaction[6] or direct correlation with the Buchner acids of known[6] structure remained to be considered as means of structure proof of the isomeric alkyltropilidenes, but fortunately a communication[7] appeared at this time describing the preparation of 1-, 2- and 3-methyltropilidenes by solvolysis of 1- and 2-methyl-1,4-dihydrobenzyl tosylates and the isomerization of the 2-isomer to the 1- and 3-isomers. Assignment of structure to the 1-isomer was substantiated by its proton magnetic resonance spectrum; assignment of structure to the 2- and 3-isomers was based on mechanistic considerations. These workers also determined the relative retention times of the 2-, 3- and 1-methyltropilidenes to be 0.50, 0.57 and 0.67, respectively, relative to *o*-xylene as 1.00 on a γ-methyl-γ-nitropimelonitrile column at 70°.[8] The 7-methyl isomer (see below) has a retention time of 0.42 on this scale so that the means of separation and identification of the isomers was readily available.

The isomer that arises from the action of methylmagnesium iodide on tropylium perchlorate was taken to be 7-methyltropilidene, by analogy with the course of the reaction with phenyllithium[9] and from mechanistic considerations. Further indication of the correctness of this assignment was gained from the identity of 7-ethyltropilidene prepared by two different routes: by the reduction of the tosylate of 2-tropylethanol[2] and by the action of ethylmagnesium bromide on tropylium perchlorate. In this connection, advantage was taken of the

(1) Presented before the Division of Organic Chemistry, 138th National American Chemical Society Meeting, New York, N. Y., September, 1960; Abstracts p. 6-P.

(1a) Department of Chemistry, Kansas State University, Manhattan, Kansas.

(2) Kenneth Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959).

(3) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958).

(4) $SnCl_4$: D. Bryce-Smith and N. A. Perkins, *Chemistry & Industry*, 1022 (1959). PCl_5: ref. 23; Br_2: W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957).

(5) *Cf.* M. J. S. Dewar, D. R. Ganellin and R. Pettit, *J. Chem. Soc.*, 55 (1958).

(6) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, *J. Am. Chem. Soc.*, **78**, 5448 (1956).

(7) N. A. Nelson, J. H. Fassnacht and J. U. Piper, *ibid.*, **81**, 5009 (1959).

(8) N. A. Nelson, private communication. I am deeply indebted to Dr. Nelson for his assistance in this important matter of isomer identification.

(9) W. von E. Doering and H. Krauch, *J. Am. Chem. Soc.*, **76**, 3203 (1954); *Angew. Chem.*, **68**, 661 (1956).

facile cleavage of tropyl ethyl ether by Grignard reagents.[10a] This cleavage is in accord with the facile cleavage of the ether by dilute mineral acid. The use of strong bases in the preparation of tropyl alkyl ethers[10b] is unnecessary; it suffices to basify an aqueous alcoholic solution of tropylium ion.

Three possible mechanisms of isomerization of 7-methyltropilidene under the influence of an electrophilic reagent were considered for detailed investigation. These are: (1) Reversible hydride exchange[11]: Abstraction of a hydride from the methylene position of a methyltropilidene would give a methyltropylium ion which could in turn abstract a hydride ion from the electrophile hydride or from a new molecule of tropilidene. Since the methyltropylium ion would be expected to accept a hydride more or less at random with respect to its methyl substituent, this mechanism would lead to a mixture of the isomeric methyltropilidenes. (2) Prototropy: Attack by a proton on the conjugated double bond system followed by loss of a proton from the methylene position of the tropilidene ring would lead to isomerization. (3) 1,2-Shift: Attack by an electrophile on the conjugated double bond system to form either a π- or a σ-complex, then a 1,2-shift of hydrogen or alkyl on the methylene carbon of the tropilidene ring to the adjacent position, and loss of the same electrophile would also give isomerization.

The isomerization of 7-methyltropilidene in acetonitrile solution was effected readily by tropylium perchlorate. The occurrence of hydride transfer was at once evident from the appearance of tropilidene. The isomeric methyltropilidenes began to form as tropilidene reached a steady state concentration and the amount of 7-methyl isomer continued to decrease even after this steady state obtained. This observation indicates that methyltropylium ion is both being formed by hydride transfer from 7-methyltropilidene and destroyed by accepting a hydride ion; *i.e.*, that it is involved in a reversible hydride exchange reaction.

After the methyltropilidene isomer mixture had come to equilibrium, the composition of the equilibrium mixture was determined. Examination of the relative amounts of the 1-, 2- and 3-isomers in aliquots during the reaction and comparison of them with the equilibrium values suggested that the 2-isomer is produced kinetically in higher proportion than its equilibrium value while the 1-isomer is produced in less than its equilibrium proportion. Since this effect only barely exceeded the experimental error of the analytical method,[12] a study of the hydride transfer to methyltropylium ion under entirely kinetically controlled conditions was undertaken. Reduction of methyltropylium ions with various complex metal hydrides appeared to be essentially instantaneous, so no electrophile long remains available to isomerize the products. Thus, the composition of the methyltropilidene mixture from such reductions reflects the product distribution in a kinetically controlled hydride transfer reaction.

Although there were variations in the relative amounts of the isomers according to the hydride used (see Table I), it was uniformly true that the 2-isomer was produced in excess of its thermodynamic proportion while the 1-isomer was produced in less than its thermodynamic proportion. Thus it appears that the kinetically produced isomer ratio in the tropylium ion catalyzed isomerization is consistent with a hydride transfer mechanism and this fact is adduced as additional support for the mechanism.

TABLE I

ISOMER COMPOSITION OF METHYLTROPILIDENE MIXTURE FROM VARIOUS SOURCES

Source	Percentage composition (±2% relative) 7-	2-	3-	1-
$LiAlH_4$, large excess in ether, $C_7H_6CH_3^+ClO_4^-$ added as solid	17.7	23.8	16.6	42.0
$LiAlH_4$, *ca.* 1 equiv. in ether, added to $C_7H_6CH_3^+ClO_4^-$ suspension in ether	6.7	27.2	18.2	48.0
$(C_6H_5)_2SnH_2$ in ether added to $C_7H_6CH_3^+ClO_4^-$ suspension in ether	0.9	26.8	19.8	52.6
$LiAl(O\text{-}t\text{-}C_4H_9)_3H$, $C_7H_6CH_3^+ClO_4^-$ diglyme suspensions mixed	...	25.1	21.5	53
$NaBH_4$ in CH_3CN soln.; $C_7H_6CH_3^+ClO_4^-$ in CH_3CN soln. added	2.1	20.8	16.2	60.8
$NaBH_4$ in aq. soln.; $C_7H_6CH_3^+ClO_4^-$ in aq. soln. added	3.7	20.4	15.2	60.6
$NaBH_4$ in aq. soln. added to $C_7H_6CH_3^+ClO_4^-$ in aq. soln.	3.8	19.7	15.4	61.3
CaH_2 suspension in CH_3CN; $C_7H_6CH_3^+ClO_4^-$ added as solid	1.0	22.4	12.3	64.4
$C_7H_7^+$ equilibration	4.6	9.6	16.1	69.7

A statistical attack of hydride ion on the methyltropylium ion would lead to an isomer composition of 14.3% of the 7- and 28.6% of each of the 1-, 2- and 3-isomers. Since the methyl group is electron releasing relative to benzene, it is surely electron releasing relative to the positively charged tropylium nucleus. Because of the polarity of the ion produced by this electron release, one would expect hydride attack to occur predominantly at or near the carbon bearing the methyl group. The carbon bearing the methyl group is, however, sterically protected. The relative amounts of deviation from the statistical distribution of hydride attack increase (algebraically) in the order 3-, 2-, 1-, as predicted by the polarity effect, and the 1- and 7-isomers combined always are produced

(10) (a) During the preparation of this paper, this type of reaction was described by H. J. Dauben, *et al.*, *J. Am. Chem. Soc.*, **82**, 5593 (1960); (b) *cf.* also W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

(11) While hydride abstractions from tropilidenes (H. J. Dauben, *et al.*, *ibid.*, **79**, 4557 (1957)) and by tropylium ion (*inter alia:* T. Ikemi, T. Nozoe and H. Sugiyama, *Chemistry & Industry*, 932 (1960)) are well known processes, no reversible hydride exchange reactions involving this system were reported until after the work described in this paper was essentially complete (see ref. 1), when a communication describing reversible hydride exchange in the tropylium system appeared: Z. N. Parnes, M. E. Vol'pin and D. N. Kursanov, *Tetrahedron Letters*, **21**, 20 (1960).

(12) The vapor chromatographic analyses of the relative amounts of the 1-, 2- and 3-isomers are very imprecise during the first part of the reaction because of the small areas of the peaks. The analyses improve in accuracy as these isomers accumulate, but the isomer composition approaches the equilibrium composition at the same time.

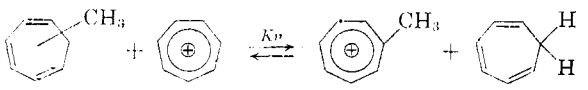
in larger amount than the 2- and 3-isomers combined, also as predicted by the polarity effect.

It is noteworthy that those hydrides which are expected to have the largest steric requirement, lithium tri-*t*-butoxyaluminum hydride, diphenyltin dihydride and (solid) calcium hydride, gave the least amount of 7-isomer (which results from attack at the carbon bearing the methyl group).

When solid methyltropylium perchlorate was added to excess lithium aluminum hydride solution, the most nearly statistical ratio of products was formed. This is as expected of the most powerful (least discriminating) of the hydrides used. The fact that in the metal hydride reductions the 2-isomer is consistently produced in higher amount than the 3-isomer, while the 3-isomer predominates in the equilibrium mixture indicates that the product distribution does not simply reflect the thermodynamic stabilities of the products. This is as expected for such exothermic reactions.

Decomposition was obvious during the hydride exchange reaction between 7-methyltropilidene and tropylium ion. The solution became appreciably dark in about one half-life (eight hours, under the conditions used). Presumably this decomposition is due to the presence of methyltropylium ion in the solutions; neither the hydrocarbons nor tropylium ion itself darkens in separate solutions under the same conditions, while methyltropylium perchlorate darkens rapidly even in the crystalline state on exposure to the atmosphere. Even though precautions were taken to exclude air and moisture from the solutions, this never was done rigorously enough to check this decomposition. If decomposition is taken as an indication of contamination by moisture or other nucleophile, one must then take into account the probability that these nucleophiles will react with methyltropylium ion or tropylium ion to remove one of them preferentially from the reaction mixture being investigated.

In order to minimize the uncertainties due to decomposition, separate experiments, of a maximum duration of seven hours, were performed to determine the position of the hydride exchange equilibrium between the equilibrium mixture of methyltropilidenes and the tropylium ion. Even so, the effect of decomposition and of nucleophiles diverting tropylium ions from the desired equi-



libration is to render the value measured for the equilibrium somewhat uncertain. Due to the moderately large value of the equilibrium constant, small variations in analyses or in the amount of extraneous nucleophile present have a large effect on the equilibrium constant. In two measurements of the composite equilibrium constant, K_n, for hydride exchange between the equilibrium mixture of *all* the methyltropilidenes and tropylium ion, values of 18 ± 4 (from the right) and 33 ± 7 (from the left) were obtained. The uncertainties express the analytical uncertainties. The difference in the values must reflect the difference in extraneous nucleophile concentration or in decomposition during the equilibrations, since the values actually have crossed over each other from the starting positions. An average value of K_n = 25 was used in the calculations which follow.

Knowledge of the composition of the equilibrium mixture of methyltropilidenes allows one to calculate the equilibrium constants between the isomers and, thence, the free energy differences between the isomers. The results of this calculation are presented graphically on the left side of Fig. 1.

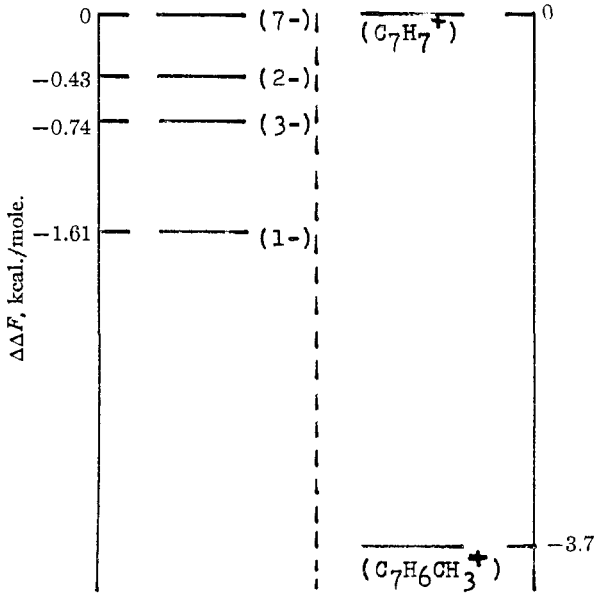
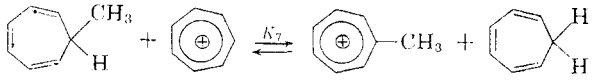


Fig. 1.—Relative free energies of the isomeric methyltropilidenes (left), and tropylium and methyltropylium ions (right). Note that 7-methyltropilidene and tropylium ion are not claimed to be equi-energetic; the chart merely represents two different energy scales whose origins have been translated in such a way that the representation is more instructive.

With a knowledge of the equilibrium constant between the isomers and the equilibrium constant between the mixed methyltropilidenes and tropylium ion, it is possible to calculate the equilibrium constant for hydride exchange between each isomeric methyltropilidene and tropylium ion. If one assumes that the resonance energy of 7-methyltropilidene is equal to that of tropilidene itself (probably true within 0.3 kcal./mole) and that there are no preferential solvation or ion pairing effects, one can ascribe the entire free energy change for the reaction involving the 7-isomer only to the difference in free energy between



tropylium ion and methyltropylium ion. On this basis, methyltropylium ion is stabilized to the extent of 3.7 ± 0.4 kcal./mole relative to the tropylium ion. The free energy relationships are presented graphically in Fig. 1. A glance at the diagram makes it evident that substituting a methyl group for a hydrogen stabilizes the tropylium ion to a much greater extent than it sta-

bilizes tropilidene. More highly methyl substituted tropilidenes should therefore be thermodynamically more effective hydride donors, while tropylium ion should be a more effective hydride acceptor, thermodynamically, than its alkylated homologs.

It is instructive to compare the stabilization produced by the substitution of a methyl group on the tropylium ion with the stabilization effected by similar substitution in other stable carbonium ions and carbonium ion intermediates (as estimated by the difference in free energies of activation of the corresponding solvolysis or substitution reaction). Comparison of the dissociation equilibria of triphenylmethyl chloride and tris-(*p*-tolyl)-methyl chloride in nitromethane[13] and in liquid sulfur dioxide[14] leads to values of 0.93 and 0.52 kcal./mole, respectively, for the stabilization of the trityl carbonium ion per methyl group. The pK_R^+ values of triphenylcarbinol and tris-(*p*-tolyl)-carbinol[15] lead to a value of 1.40 kcal./mole for the stabilization per methyl group in sulfuric acid solution. The partial rate factors for bromination, chlorination and acetylation[16] of toluene in the *p*-position[17] give stabilizations of the intermediate ion of 4.6, 4.0 and 3.9 kcal./mole, respectively. The stabilization of the allyl carbonium ion by methyl substitution at the γ-atom in solvolyses in formic acid[18] amounts to about 5.3 kcal./mole. The average stabilizing effect of each additional methyl group in the series methyl, ethyl, isopropyl and *t*-butyl carbonium ions in the gas phase amounts to 28 kcal./mole.[19]

Evidently, methyl substitution makes the largest contribution to stabilization of the carbonium ion when other means of stabilization (delocalization, solvation) are at a minimum, but makes a much smaller contribution when the carbonium ion is already highly stabilized by extensive delocalization. More quantitatively, the amount of stabilization decreases monotonically as the delocalization is extended from a 1-atom system (28 kcal.), a 3-atom system (5.3 kcal.), a 5-atom system (4.2 kcal.), a 7-atom system (3.7 kcal.) to a 19-atom system (*ca.* 1 kcal./methyl group). While this smooth monotonic decrease is possibly fortuitous in view of the wide range of media, carbonium ion geometry and types of observation from which the data are derived, the general trend is undoubtedly significant.

The hydride exchange reaction between 7-methyltropilidene and tropylium ion was examined kinetically as well. Unfortunately, the decomposition which accompanies the hydride exchange reaction and the probable presence of extraneous nucleophiles do not permit one to obtain very accurate rate constants, nor to establish the kinetic order with any certainty. The disappearance of the 7-methyltropilidene was approximately pseudo-first order with respect to itself. The pseudo-first order rate constant showed only a slight downward drift as the reaction progressed, probably because the concurrent decomposition destroyed hydride exchanging species. The concentration of tropilidene reached a steady state within the first 13% of the reaction. If one calculates the relative amounts of methyltropylium ion and tropylium ion present in the steady state from K_n, it turns out that the hydride acceptors present are ~99.5% methyltropylium ion and ~0.5% tropylium ion. Thus the rate constants obtained by dividing the pseudo-first order rate constants by the initial tropylium ion concentration (assuming the hydride exchange is first order in hydride acceptor as well as in hydride donor) are second-order rate constants for hydride exchange from 7-methyltropilidene to methyltropylium ion. The values obtained in two experiments were 3.6 and 2.7×10^{-4} l./mole-sec.

That the tropylium ion contributes only insignificantly to the total hydride exchange rate at the steady state was established in two ways. A kinetic run was made in which 7-methyltropilidene was used with triphenylmethyl carboniun ion as the initial hydride acceptor in place of the tropylium ion. Since the equilibrium constant for hydride exchange between trityl carbonium ion and methyltropylium ion will be of the order of 10^{11},[20] the contribution of trityl to the total hydride exchange rate at the steady state can be neglected. Since the rate constant obtained in this experiment was the same, 2.9×10^{-4} l./mole-sec., within experimental error, as those obtained when tropylium ion was the original source of the hydride acceptors, it follows that tropylium ion was making no significant contribution to the over-all hydride exchange rate.

By taking a number of points very early in the reaction, it was possible to measure the rate of approach of the tropilidene concentration to its steady state value. The rate constant obtained was extremely crude, probably in error by as much as a factor of three or four. Nevertheless, the value found, 1.8×10^{-3} l./mole-sec., gives an estimate of the rate at which hydride is transferred from 7-methyltropilidene to tropylium ion. When this rate is used to calculate what contribution the 0.5% of tropylium ion makes to the over-all hydride exchange rate, the earlier conclusion that its contribution is insignificant is substantiated. It appears that tropylium ion is kinetically more effective as a hydride acceptor than its methyl homolog. This kinetic effectiveness is consonant with its thermodynamically greater effectiveness as a hydride acceptor. It is also interesting to note that the rate constant for hydride exchange between tropilidene and tropylium ion in acetic acid solution at 25°, 5.3×10^{-4} l./mole-sec. (interpolated from data given in ref. 11), is in general agreement with these ideas, even though the solvent used is a different one, in that tropilidene is a

(13) A. G. Evans, *et al.*, *Trans. Faraday Soc.*, **50**, 16 (1954).

(14) P. D. Bartlett, *J. Chem. Ed.*, **30**, 22 (1953).

(15) N. C. Deno, *et al.*, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

(16) These particular reactions were chosen because the transition state in these cases probably most nearly approximates the carbonium ion intermediate.

(17) L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 5621 (1959).

(18) R. H. De Wolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

(19) D. P. Stevenson, *J. Chem. Phys.*, **10**, 291 (1942); F. P. Lossing and J. B. deSousa, *J. Am. Chem. Soc.*, **81**, 281 (1959).

(20) Compare the pK_R^+ values, 4.7 for tropylium and −6.63 for trityl: W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954); N. C. Deno, *et al.*, *ibid.*, **77**, 3044 (1955).

less effective hydride donor than methyltropilidene.

The possibility of prototropic isomerization in solutions of the range of acid concentration encountered in the study of fragmentation reactions in the tropilidene series[2] was investigated by treating an acetonitrile solution of 7-methyltropilidene with mineral acid. Difficulty was experienced during the exploratory runs in obtaining even roughly reproducible rates of isomerization. The suspicion arose that the rate depended upon the amount of oxygen in the vapor space over the solution. The supposition was checked by doing parallel runs with perchloric acid under a nitrogen atmosphere and under an oxygen atmosphere. It was found that the reaction under oxygen had proceeded at a faster rate, as shown by the isomer composition after two days. In addition it appeared that the reactions were very slow at first and gradually accelerated, as expected if the isomerization depended upon the gradual production of the active catalytic agent.

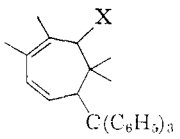
These observations are explained on the basis of oxidation by air (which was never rigorously excluded) or, partially, by the action of the oxidizing mineral acids on the methyltropilidene to produce methyltropylium ion which then served as the isomerizing agent by hydride exchange as already discussed. The initial very slow rate of isomerization in the presence of acid before the accumulation of methyltropylium ion indicates that acid-catalyzed isomerization is very slow, though the experiments do not, of course, rule out the occurrence of this mechanism entirely.

The possibility of isomerization involving a 1,2-shift was investigated using a geminal dimethyltropilidene, 2,3,7,7-tetramethyltropilidene,[21] derived from eucarvone. It was hoped that an electrophile like triphenylmethyl carbonium ion would induce a rearrangement by 1,2-methyl migration and then abstract the hydride ion thus made available to produce 1,2,4,5- or 1,2,3,4-tetramethyltropylium ion. This sort of reaction was of additional interest in view of the stabilizing influence of methyl substituents on the tropylium ion already discussed.

In fact, the reaction takes an alternate course: the trityl ion adds to the triene system and the carbonium ion thus formed reacts with the acetonitrile solvent. The nitrilium perchlorate Ia isolated reacts with aqueous base to form the corresponding amide Ib. The spectral evidence indicates the diene system (λ_{max} 237 mμ, log ϵ 4.24) and the geminal dimethyl group (ν_{max} 1375, 1390 cm.$^{-1}$). The structure I is assigned rather than the alternate one where the trityl group and the –X group are interchanged on the basis of the expected lower steric hindrance at the 6-position than at the 1-position to attack by the bulky trityl carbonium ion.

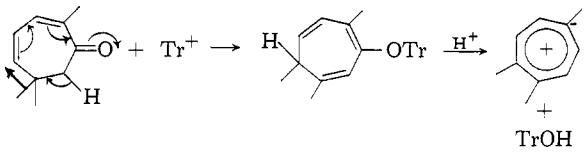
Ia, X = $-\overset{+}{N} \equiv CCH_3$ $^{-}ClO_4$

Ib X = $-NHCOCH_3$

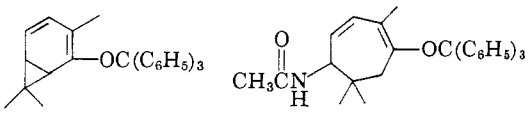


(21) E. J. Corey, H. J. Burke and W. A. Remers, *J. Am. Chem. Soc.*, **77**, 4941 (1955).

The reaction of eucarvone itself with triphenylmethyl (Tr^+) perchlorate was studied in the hope that a reaction of the type shown might occur



and that the initial product might be induced to fragment to a trimethyltropylium ion and triphenylcarbinol. In fact, two products were isolated from the reaction, but the ultraviolet spectra indicated that these were both dienes rather than tropilidenes. On this evidence it is apparent that the reaction took some other course than that involving a 1,2-shift. One of the products isolated from the eucarvone triphenylmethyl carbonium ion reaction is eucarvone enol triphenylmethyl ether II,[22] identical with material prepared by an alternate procedure. The other product appears to be an addition product involving solvent and is given the formula III.



II III

It seems that the 1,2-shift mechanism is slow relative to alternate courses of reaction and it is therefore inferred that this mechanism contributes slightly, if at all, to the isomerization of methyltropilidene.

Experimental

Melting points were taken in capillary tubes and are corrected; boiling points are uncorrected. Spectra were determined by Miss Donna Karasek on a Cary model 11 or on a Perkin–Elmer model 21. The microanalyses were done by Miss Heather King.

Tropylium perchlorate was prepared by a slight modification of the method described by Kursanov and Vol'pin[23] on a 1/4 mole scale. Tropylium perchlorate serves as well as tropylium bromide in all the condensation reactions reported earlier[2] and is preferable both for its ease of preparation and for its better keeping qualities. Tropylium perchlorate can be recrystallized from 1% perchloric acid on a small scale if one works rapidly. In future work, use will be made of tropylium fluoroborate[23b] to avoid the possibly serious hazard of working with the perchlorate, although no untoward incidents have occurred in this work.

Tropyl Ethyl Ether (7-Ethoxycycloheptatriene).[24]—To a vigorously stirred solution of 20 g. of crude tropylium perchlorate (*ca.* 105 mmoles) in 10 ml. of 95% ethanol and 50 ml. of water was added 10.5 g. (*ca.* 125 mmoles) of sodium bicarbonate as rapidly as the foaming allowed. After a few minutes the oily layer was collected with the aid of ether, the ether layer dried over magnesium sulfate, concentrated and the residue distilled to give 10.55 g. (74%) of colorless oil, b.p. *ca.* 62° (8 mm.), $n^{23}D$ 1.4990.

Anal. Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.32; H, 8.76.

(22) See K. Conrow, *ibid.*, **82**, 5504 (1960), for assignment of structure II.

(23) (a) D. N. Kursanov and M. E. Vol'pin, *Doklady Akad. Nauk SSSR*, **113**, 339 (1957); *C. A.*, **51**, 14572e (1957); (b) G. Fraenkel, R. E. Carter, A. McLachlan and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5847 (1960).

(24) Throughout this and the preceding paper,[2] the convention has been adopted that "tropyl" or "cycloheptatrienyl" refers to "1,3,5-cycloheptatrien-7-yl" and not to "2,4,6-cycloheptatrien-1-yl."

A solution of 0.17 g. of tropyl ethyl ether in 15 ml. of ether was extracted with three 5-ml. portions of 1 *N* hydrochloric acid. The extracts were treated with excess pentane-2,4-dione and basified with sodium bicarbonate. Tropylacetylacetone (0.19 g., 80%) precipitated.

7-Methyltropilidene (7-Methylcycloheptatriene).[25]—To a stirred solution of methylmagnesium iodide prepared from 3.4 g. (140 mmoles) of magnesium turnings and 4.4 ml. of methyl iodide in 200 ml. of anhydrous ether was added 19.0 g. (100 mmoles) of finely powdered tropylium perchlorate. After 2 hours, the mixture was poured onto a mixture of ice and ammonium chloride and the ether layer was collected, dried over magnesium sulfate, concentrated and distilled through a Holzman column to give 7.79 g. (74%) of colorless liquid, b.p. *ca.* 55° (50 mm.), $n^{25}D$ 1.5016. Vapor phase chromatography of the center cut showed greater than 99% purity.

7-Methyltropilidene (from Tropyl Ethyl Ether).—To a solution of methylmagnesium iodide prepared from 1.68 g. (70 mmoles) of magnesium and 4.7 ml. (75 mmoles) of methyl iodide in 70 ml. of ether, was added 6.99 g. (51.3 mmoles) of tropyl ethyl ether dropwise. Each drop caused a vigorous boiling of the solution. The mixture was stirred 20 minutes after the addition was complete and then worked up by pouring into ammonium chloride solution. The ether layer was washed with *N* hydrochloric acid to remove any unreacted tropyl ethyl ether, dried with magnesium sulfate and distilled to give 4.05 g. (74%) of colorless liquid, *ca.* 50° (42 mm.), $n^{21}D$ 1.5029.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 89.66; H, 9.33.

7-Ethyltropilidene (7-Ethylcycloheptatriene).—This substance was prepared from tropylium perchlorate and ethylmagnesium iodide in a manner exactly analogous to that described above for the methyl homolog in 83% yield, b.p. *ca.* 63° (28 mm.).

7-Ethyltropilidene (from 2-Tropylethanol[2]).—A mixture of 1.93 g. (14.2 mmoles) of tropylethanol, 2.97 g. (15.6 mmoles) of tosyl chloride and 5.0 ml. of pyridine was prepared at 0° and kept overnight at 0°. The mixture was poured into ice-water, the oil collected with the aid of ether and the ether solution washed with *N* hydrochloric acid. The ether layer was dried over magnesium sulfate before being added to 0.67 g. (17.5 mmoles) of lithium aluminum hydride in dry ether. After stirring at room temperature for 2 days, the mixture was worked up by the addition of 1.33 ml. of water and 1.00 ml. of 10% sodium hydroxide solution, filtration, drying, concentration and distillation through the Holzman column to give 0.98 g. (58%) of colorless oil, b.p. *ca.* 55° (19 mm.). This substance gave an identical infrared spectrum and showed identical vapor phase chromatographic behavior with the sample prepared by the earlier method.

Anal. Calcd. for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.87; H, 10.19.

Pyrolysis of 7-Ethyltropilidene.—A solution of 1.00 ml. of 7-ethyltropilidene in 25 ml. of pentane was allowed to drop slowly through a vertical stainless steel helices packed tube (an old one; carbonaceous material from previous pyrolyses was present) during an hour and a half, while the tube was held at 400°. The pyrolysate was collected and redistilled to give 0.67 g. of colorless oil, b.p. 75–85° (40 mm.). Vapor phase chromatography gave four distinct peaks in an approximate ratio of 4:5:6:1 in the order of elution from the γ-methyl-γ-nitropimelonitrile column. Combination of this mixture with one obtained by the hydride exchange method (see below) gave the same four peaks. *n*-Propylbenzene has a retention time which differs only slightly from one of these four peaks, so one cannot be sure of its absence, though it appeared not to be present in any quantity.

Methyltropilidene Isomer Identification and Vapor Phase Chromatography Controls. Retention Times.—Nelson[8] reported that the retention times of the 2-, 3- and 1-methyltropilidenes on a γ-methyl-γ-nitropimelonitrile column at 70° relative to *o*-xylene as 1.00 were, respectively, 0.50, 0.57 and 0.67. 7-Methyltropilidene was found to have a relative retention time of 0.42 and tropilidene itself 0.39 under these same conditions. The aliquots resulting from tropylium ion-catalyzed isomerization of 7-methyltropilidene (see below) gave peaks at 0.39, 0.42, 0.50, 0.57 and 0.65 relative to *o*-xylene. These peaks are ascribed to tropilidene and the 7-, 2-, 3- and 1-methyltropilidenes, respectively.

Area Calibration.—A mixture of 79.2 mg. of pure tropilidene (0.859 mmole) and 80.0 mg. of mixed methyltropilidenes (0.753 mmole) was chromatographed at 120° on a didecyl phthalate column. The $C_7H_8/C_7H_7CH_3$ area ratio was 0.98. The correction factor by which the area ratio is to be multiplied to obtain the mole ratio works out to be 1.16. In a second experiment, 64.3 mg. of 93.5% mixed methyltropilidenes (0.564 mmole) and 57.2 mg. of 92% tropilidene–8% toluene mixture (0.620 mmole) gave an area ratio of 1.01, which leads to a correction factor of 1.09. Thereafter the $C_7H_8/C_7H_7CH_3$ area ratio measured was multiplied by 1.13 to obtain the molar ratio of these substances.

Extraction Control.—A mixture of benzene and 7-methyltropilidene (10 μl.) was dissolved in 0.33 ml. of acetonitrile, the solution added to 1.0 ml. of pentane and the pentane layer washed with two 2-ml. portions of 1 *N* hydrochloric acid. The pentane layer was analyzed directly; it contained no acetonitrile and showed the same ratio of benzene/7-methyltropilidene as did the original mixture.

Tropylium Ion-catalyzed Isomerization of 7-Methyltropilidene (Run I).—A solution of 395.2 mg. (2.08 mmoles) of recrystallized tropylium perchlorate and 1.00 ml. of benzene in 20.0 ml. of acetonitrile (distilled from phosphorus pentoxide and stored over molecular sieves) was prepared in a 25-ml. erlenmeyer flask fitted with a serum cap. The flask was swept with nitrogen, capped and equilibrated at 25.0° before 1.925 g. (18.1 mmoles) of 7-methyltropilidene was injected by means of a hypodermic syringe. An immediate light orange coloration resulted. Aliquots of 0.33 ml. were withdrawn at intervals by means of a hypodermic syringe and added to 1 ml. of pentane and 2 ml. of 1 *N* hydrochloric acid. The pentane layer was washed once more with 2 ml. of 1 *N* hydrochloric acid before being analyzed on the nitromethylpimelonitrile column with a recorder equipped with an integrator. Tropilidene appeared as a shoulder on the 7-methyltropilidene peak which had attained a constant height in 20 min. (*ca.* 13% of reaction). In the later stages of the reaction when 7-methyltropilidene had decreased to a concentration equivalent to that of tropilidene, resolution into two peaks occurred. The height of the first peak was the same as that of the shoulder and its area could be determined. The area of the 7-methyltropilidene peak was found by subtracting this (steady state) area for tropilidene from each of the areas found in the earlier points for the combined tropilidene–7-methyltropilidene peak. The combined areas of all the methyltropilidene peaks were normalized to 100; the normalized area of the benzene peak was about 53 at the beginning of the run and about 67 at the end, indicating that the decomposition which was obvious visually had proceeded to the extent of about 21% as measured by the loss of methyltropilidenes.

Attempts to calculate a rate constant from the time of injection of the 7-methyltropilidene gave very poor results; when t_0 was taken after tropilidene had attained its steady state concentration (in 20 minutes), the rate constant showed only a slight downward drift (to about 65% of its initial value), probably due to the decomposition which occurred simultaneously. Representative points are given in Table II, along with the average rate constant based on 24 points ranging from 6 to 94% of completion based on the new t_0. Dividing k_1 by the tropylium ion concentration gives a second-order rate constant $k_2 = 3.6 \pm 0.4 \times 10^{-4}$ l./mole-sec.

Tropylium Ion-catalyzed Isomerization of 7-Methyltropilidene (Run II).—A solution of 190.7 mg. (1.000 mmole) of recrystallized tropylium perchlorate in 10.0 ml. of acetonitrile (which had been distilled from phosphorus pentoxide and stored over a month in a glass stoppered bottle) was prepared as above before injection of 937.0 mg. of 95.5% 7-methyltropilidene (8.42 mmoles). Aliquots were taken after 1, 4, 7, 10, 20 and 30 minutes and analyzed on the didecyl phthalate column for tropilidene. The rate of hydride transfer to tropilidene was calculated from the expression $k = x_{eq}/at \ln (x_{eq}/x_{eq} - x)$ where x_{eq}/a was taken to be 0.99 on the basis of the equilibrium constant measurement (x_{eq} is the normalized equilibrium area of the tropilidene peak, x is the normalized area of the tropilidene peak at time t). The rate calculated in this way drifted down by a factor of about three from the first to the last of the above

(25) E. W. Abel, *et al.*, *J. Chem. Soc.*, 4559 (1958). The different name given this substance by Abel, *et al.*, arises from their adoption of a different nomenclature convention.

TABLE II

TROPYLIUM-ION CATALYZED ISOMERIZATION RATE, RUN I

Solvent: 20.0 ml. CH_3CN; tropylium perchlorate, 395.2 mg. (*ca.* 0.0896 *M*); 7-methyltropilidene, 1.925 g. (*ca.* 2.25 ml.); temperature, 25.0°

$10^{-4}t$, sec.	x[a]	Product composition, %: 2-	3-	1-	10^5k_1[b]
0.00	95.5	29	12	59	..
.18	90.3	20	17	63	3.2
.60	78.3	17	23	61	3.4
.96	69.0	14	20	66	3.4
1.32	64.0	15	18	66	3.1
2.04	51.0	15	19	66	3.1
2.76	40.4	13	19	68	3.2
4.20	28.6	13	18	69	3.0
10.68	9.8	11	18	71	2.5
∞	4.2	9.9	16.4	73.7	..
		Av. k_1 (of 24 points, see text)			3.2 ± 0.3

[a] Normalized area (x) of 7-methyltropilidene peak on v.p.c. (see text). [b] Calcd. using: $k_1 = \frac{(a - x_{eq})}{t\ a} \ln \frac{(a - x_{eq})}{(x - x_{eq})}$ where $a = x_0 = 95.5$ and $x_{eq} = 4.2$.

points, using the time of injection of the 7-methyltropilidene at t_0. Dividing the average rate "constant" by the 7-methyltropilidene concentration gives a second-order rate constant $k_2 = 1.8 \pm 0.6 \times 10^{-3}$ l./mole-sec.

Determination of the pseudo-first-order rate constant for the disappearance of 7-methyltropilidene was done in the same way as in run I except that the areas were determined by multiplying the height of the peak by the width at half the height and t_0 was taken 30 minutes after the 7-methyltropilidene injection. The k_2 obtained was $2.7 \pm 0.3 \times 10^{-4}$ l./mole-sec. The most likely explanation for the fact that these determinations differ by more than their average deviations is that there was a different amount of decomposition and/or diversion of tropylium ions by extraneous nucleophiles.

The values reported in Table I for the product composition at infinity are the average of seven determinations taken at four different times at infinity from run I and three from run II. It has been assumed that the areas of the various methyltropilidene peaks are proportional to the mole fractions of the isomers and that the decomposition has not affected the relative amounts of the isomers. This last assumption seems justified by the observation that the isomer ratios at infinity are unchanged during 24–36 hours of continued decomposition.

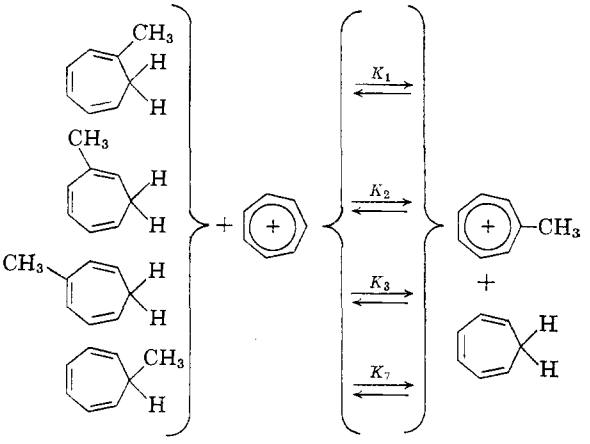
Triphenylmethyl Carbonium Ion-catalyzed Isomerization of 7-Methyltropilidene.—To a solution of 351.6 mg. (1.02 mmoles) of freshly prepared ether-washed and vacuum-dried trityl perchlorate in 10.0 ml. of dry acetonitrile thermostated at 25.0° in a nitrogen-swept, serum-capped vial was added 896.7 mg. (8.44 mmoles) of pure 7-methyltropilidene. Aliquots were withdrawn as before and analyzed as in run II. The rate constant showed the usual downward drift and, upon division by the initial trityl ion concentration, turned out to be $2.9 \pm .4 \times 10^{-4}$ l./mole-sec. The 2-isomer was, as before, produced in more than its equilibrium ratio, while the 1-isomer was produced in less than its equilibrium ratio.

Methyltropylium Perchlorate.[26]—To a suspension of 0.90 g. (*ca.* 2.6 mmoles) of triphenylmethyl perchlorate in 5.0 ml. of acetonitrile was added 0.31 ml. (*ca.* 2.5 mmoles) of 7-methyltropilidene. The color was essentially discharged in 5 minutes. The mixture was evaporated *in vacuo* at room temperature, 15 ml. of ethyl acetate was added and the mixture again evaporated to dryness. The solid was triturated with 15 ml. of fresh ethyl acetate and collected by filtration and immediately dried *in vacuo* in a drying pistol. The substance decomposes rapidly on exposure to air; yield 0.46 g., 90%, m.p. 111–112°, lit.[26] m.p. 109°.

Tropilidene, Methyltropylium Perchlorate Equilibration.—A solution of 52.4 mg. (0.568 mmole) of pure tropilidene (see below) and 101 mg. (0.494 mmole) of methyltropylium perchlorate in 1.00 ml. of acetonitrile was thermostated at 25.0°. Aliquots of 0.33 ml. were taken after 2 hr., 4.25 hr. and 7 hr. The tropilidene/methyltropilidene ratios (as determined on didecyl phthalate) were the same, within experimental error, for the 4.25- and 7-hour aliquots and the ratio of 2-, 3- and 1- methyltropilidenes (as determined on the nitromethylpimelonitrile column) was the equilibrium ratio for the 7-hour aliquot. The average value for the area ratio in the 4.25-hr. and 7-hr. aliquots was 4.12 (C_7H_8/C_7H_7-CH_3). A value of $K_n = 18$ is calculated from this value.

Mixed Methyltropilidene, Tropylium Perchlorate Equilibration.—A solution of 192.9 mg. (1.01 mmoles) of recrystallized tropylium perchlorate and 120.0 mg. of 93.5% mixed methyltropilidenes (1.06 mmoles) in 2.0 ml. of dry acetonitrile was prepared in a serum-capped nitrogen-swept vial by intermittent stirring until solution was complete. The mixture was thermostatted at 25°. Samples taken after 2 hours showed no further change in the area ratio, whose average value was 4.37. The value of K_n calculated from this turns out to be 33.

Calculation of Equilibria and ΔF's.—Using the scheme



it follows from the observed isomer distribution at equilibrium (Table I) that $K_1/K_7 = 0.066$, $K_2/K_7 = 0.477$, $K_3/K_7 = 0.286$, whence the free energy differences between the respective pairs of isomers are 1.61, 0.43 and 0.74 kcal./mole. The composite equilibrium constant, K_n, for the equilibrium mixture of the methyltropilidenes reacting with tropylium ion $= 1/(1/K_1 + 1/K_2 + 1/K_3 + 1/K_7)$ or $0.0460\ K_7$. Since $K_n = 25$, it follows that $K_1 = 35$, $K_2 = 255$, $K_3 = 153$ and $K_7 = 535$, and hence $\Delta F_7 = -3.72$ kcal./mole.

Estimation of the Uncertainties in ΔF's.—It was assumed that there could be 2.5% errors in the area measurements. Since the area measurements are involved in the factor by which the area ratio was multiplied to obtain the mole ratio, it was considered that this could have the maximum and minimum values of 1.18 and 1.07. The area ratios measured from the vapor phase chromatograms of the equilibration studies were given similar maximum and minimum values based on the same assumption. (The analyses all fell within this tolerance in each run.) The area ratios in the analyses of the relative amounts of the methyltropilidene present at the end of the rate runs were found to vary by more than this tolerance in the case of the 7-isomer, because it is present in such small amount. The percentage of each isomer was assumed to vary between the following extremes: 4.0 and 5.2%, 9.25 and 10.05%, 15.4 and 16.8%, and 68.65 and 70.75% for the 7-, 2-, 3- and 1-isomers, respectively. Then the entire calculation of the ΔF's was repeated using those sets of extreme values of the correction factor (1.18 or 1.07), K_n (16 or 39) and the isomer percentages (see above) which would give maximum and minimum values of ΔF for each particular case. The extreme values obtained for each of the quantities represented in Fig. 1 were: 0.34 and 0.55, 0.64 and 0.85, 1.53 and 1.70, and 3.39 and 4.08 kcal./mole. The isomer free energy differences can thus be assigned uncertainties of ±0.1 kcal./mole, while the tropylium ion methyltropylium ion free energy difference can be assigned an uncertainty of ±0.4 kcal./mole.

Sodium Borohydride Reduction of Tropylium Perchlorate.—To a solution of excess sodium borohydride in 5 ml. of water covered with 5 ml. of pentane was added slowly 1.10 g. (5.8 mmoles) of tropylium perchlorate. The excess boro-

(26) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, *J. Am. Chem. Soc.*, 79, 4557 (1957).

hydride was destroyed by adding formalin. The pentane layer was separated and washed with water, dried over magnesium sulfate, concentrated through a Holzman column and distilled in a micro-still. The sample collected at 65° (130 mm.) amounted to 0.31 g. (58%) and was homogeneous to vapor phase chromatography. This method is recommended as a convenient way to make toluene-free tropilidene.

Metal Hydride Reductions of Methyltropylium Perchlorate.—The solvents and hydrides used have been summarized in Table I. When ether was used as the solvent, the reaction was quenched with 1 *N* hydrochloric acid and the ether solution analyzed directly by v.p.c. When acetonitrile or diglyme was the solvent, the mixture was poured into 1 *N* hydrochloric acid, the hydrocarbons extracted with pentane and the extract washed with more hydrochloric acid and analyzed. The aqueous reductions were simply acidified and extracted with pentane for analysis.

Sulfuric Acid-catalyzed Isomerization of 7-Methyltropilidene.—A solution of 0.535 ml. of concentrated sulfuric acid and 1.00 ml. (*ca.* 10 mmoles) of benzene in 20.0 ml. of dry acetonitrile was placed in a 25-ml. erlenmeyer flask, the vapor space swept with nitrogen, capped with a serum cap and thermostated at 25.0°. Then 2.025 g. of 7-methyltropilidene (19.1 mmoles) was added by means of a hypodermic syringe. An immediate light yellow coloration was produced which darkened as time went on. The mixture separated into two phases within 24 hours. Aliquots withdrawn as before showed no appearance of isomeric tropilidenes in the first 3 hours. An aliquot from the larger (upper) phase after 24 hours indicated that the reaction had progressed to the extent of about 40% in this time. On the basis of this result and the assumption of a pseudo-first order reaction, the reaction should have progressed to the extent of 6.5% in the first 3 hours, but the analyses clearly showed that this had not been the case.

Perchloric Acid-catalyzed Isomerization of 7-Methyltropilidene.—Two identical solutions of 0.206 ml. of 70% perchloric acid (*ca.* 2.5 mmoles) and 0.55 ml. of 7-methyltropilidene (*ca.* 3 mmoles) in 5.0 ml. of acetonitrile were prepared in serum-capped vials. One vial was flushed with nitrogen before capping, the other with oxygen. After 2 days at room temperature, the isomerization under nitrogen had proceeded to the extent of 57% and the one under oxygen to the extent of 80%.

N-(5-Triphenylmethyl-1,2,6,6-tetramethylcycloheptadien-7-yl)-acetonitrilium Perchlorate.—To a suspension of 2.31 g. (6.75 mmoles) of freshly prepared trityl perchlorate in 20 ml. of dry acetonitrile was added 1.15 ml. (*ca.* 6.75 mmoles) of 2,3,7,7-tetramethyltropilidene.[21] There was an immediate formation of a darker red color, then gradual dissolution of the trityl perchlorate, finally a lightening in color and a gradual precipitation of white crystals, which were collected after an hour. A second crop was obtained by evaporation, addition of ethyl acetate, evaporation, trituration with ethyl acetate and filtration; combined wt., 1.68 g. (47%). The substance was recrystallized from dry acetonitrile, from which it recrystallized very slowly to give colorless micro-crystals, m.p. 213–215° dec.; ν_{max}^{KBr} 1493, 1592, 700, 740, 760, (triphenylmethyl), 1450, 1375, 1390 (geminal dimethyl), 1680 (nitrilium ion), 1025–1125 cm.$^{-1}$ (perchlorate ion); $\lambda_{max}^{CH_3CN}$ 237 mμ (log ϵ 4.24).

Anal. Calcd. for $C_{32}H_{34}ClNO_4$: C, 72.23; H, 6.44. Found: C, 71.98; H, 6.64.

N-(5-Triphenylmethyl-1,2,6,6-tetramethylcycloheptadien-7-yl)-acetamide.—To a solution of 0.25 g. of the acetonitrilium perchlorate in 5 ml. of hot acetonitrile was added cautiously 1 ml. of 5% sodium bicarbonate solution. Then 25 ml. of water was added. The white precipitate was collected and recrystallized from absolute ethanol to give white prisms, m.p. 150.5–151.5°; ν_{max}^{KBr} 1493, 740, 760, 700 (triphenylmethyl), 1450, 1372, 1385 (geminal dimethyl), 3160, 1658 (amide) cm.$^{-1}$; λ_{max}^{EtOH} 236 mμ (log ϵ 4.21).

Anal. Calcd. for $C_{32}H_{25}NO$: C, 85.48; H, 7.85; N, 3.12. Found: C, 84.90; H, 8.19; N, 2.93.

This substance appeared to deteriorate on standing. Attempts to prepare new samples or to purify them further gave lower melting points and poorer analyses.

Reaction of Eucarvone and Triphenylmethyl Perchlorate.—To a suspension of about 7 mmoles of freshly prepared triphenylmethyl perchlorate in 20 ml. acetonitrile was added 1.15 ml. (*ca.* 7 mmoles) of eucarvone. A deep red color was produced immediately. The mixture was allowed to stand overnight, during which time the trityl perchlorate had all dissolved. The mixture was poured into 50 ml. of 5% sodium bicarbonate solution and 100 ml. of ether. The ether layer was then washed quickly with 50 ml. of 1 *N* hydrochloric acid and the aqueous layer quickly separated. The ether layer was washed several more times with 1 *N* hydrochloric acid. The combined aqueous layers slowly precipitated 1.48 g. (43%) of fluffy white crystals, m.p. 160.0–162.0° dec. Repeated crystallization from 95% ethanol does not raise the melting point; ν_{max}^{KBr} 705, 743, 762, 1493, 1590, 3040 (triphenylmethyl), 1450, 1345, 1386 (geminal dimethyl), 1658, 3360 (amide), 2500 (broad) (N–H$^+$) cm.$^{-1}$; λ_{max}^{EtOH} 231 mμ (log ϵ 4.20).

The substance gave inconsistent analytical results in general agreement with values calculated for $C_{31}H_{34}ClNO_2$: C, 76.28; H, 7.02. Found: C, 77.55, 75.04; H, 7.37, 6.86; N, 3.77. Silver chloride precipitated immediately with alcoholic silver nitrate; carbon dioxide is liberated with sodium bicarbonate solution.

The ether layer remaining after the hydrochloric acid washes was concentrated and the residue was taken up in hot 95% ethanol and allowed to cool. Off-white crystals precipitated; 1.05 g. (38%), m.p. 180–195°. Repeated recrystallization from 95% ethanol raised the melting point to 196–200°; ν_{max}^{KBr} 700, 743, 762, 1490, 1592, 3040 (triphenylmethyl), 1375, 1445 (geminal dimethyl), and 1643 (enol ether) cm.$^{-1}$; λ_{max}^{EtOH} 230 mμ (log ϵ 4.26).

Anal. Calcd. for $C_{29}H_{28}O$: C, 88.73; H, 7.19. Found: C, 88.97; H, 7.41.

A solution of this material (198 mg., 0.507 mmole) in concentrated sulfuric acid was diluted with water and steam distilled. The steam distillate was extracted with ether, the ether removed and the residue treated with a diglyme solution of 2,4-dinitrophenylhydrazine and two drops of concentrated hydrochloric acid. After standing 4 days, dilution with water gave red crystals, m.p. 145–148°, 61.1 mg. (37%), which were recrystallized from absolute ethanol to give eucarvone 2,4-dinitrophenylhydrazone, m.p. and m.m.p 150.5–152.5°, lit.[27] m.p. 152–153°. The residue from the steam distillate was filtered to give off-white crystals, 96.5 mg. (73%), m.p. 150–156°, whose infrared spectrum showed them to be impure triphenylcarbinol (m.p. 162.5°).

Eucarvone Enol Triphenylmethyl Ether.[28]—A suspension of 2.56 g. of sodamide (65 mmoles) in 125 ml. of purified dioxane and 5.70 g. (38 mmoles) of eucarvone was kept at reflux under nitrogen for 2.5 hours. Then 18.2 (65 mmoles) of chlorotriphenylmethane was added all at once to the ice-cooled solution. After an hour at reflux, the mixture was filtered, the filtrate concentrated to dryness and the residue crystallized repeatedly from ethanol containing a bit of benzene. After four crystallizations the m.p. was 188–196° and m.m.p. and infrared spectral comparison with the above material showed them to be identical; yield 10.6 g. (71%).

(27) T. F. West, *J. Chem. Soc.*, 1162 (1940).

(28) *Cf.* E. J. Corey and H. J. Burke, *J. Am. Chem. Soc.*, **78**, 178 (1956).