If we assume that the excess entropy of the *trans*-2-*t*-Bu-6-Me isomer is principally due to the mixing of the different twist conformations (I–III and VI), the contributions of the different twist forms may be estimated from the experimentally determined entropy difference (10.73 J mol^{-1} °K^{-1} = 2.56 cal mol^{-1} °K^{-1}) and the equation

$$\frac{\Delta S^\circ_{\mathrm{exptl}}}{R} = 2x \ln x + (1 - 2x) \ln (0.5 - x) \quad (1)$$

where x is the mole fraction of I and VI and $(0.5 - x)$ that of II and III. Then the proportions of I and VI will be about 36% and those of II and III about 14%. Thus the free-energy difference between I (or VI) and II (or III) is about 2.3 kJ mol^{-1} (0.55 kcal mol^{-1}).

The excess enthalpy of I and VI with respect to the unsubstituted twist conformations was assumed to amount to 2 kJ mol^{-1} (0.5 kcal mol^{-1}; see before) and hence that of II and III (if the twist forms do not differ in entropy) will be (2 + 2.3) = 4.3 kJ mol^{-1} (1.03 kcal mol^{-1}), also in close agreement with the preceding postulation.

Since

$$\Delta H = \Sigma x_i \Delta H_i$$

the total excess enthalpy of *r*-2-*tert*-butyl-2, *trans*-6-dimethyl-1,3-oxathiane will be $\Delta H^\circ_{\mathrm{CT}}$ +2.64 kJ mol^{-1} ($\Delta H^\circ_{\mathrm{CT}}$ +0.63 kcal mol^{-1}) over that of an unsubstituted chair form. The conformational enthalpy of an axial methyl group at position 2 in the 1,3-oxathiane ring has been determined (13.6 kJ mol^{-1} = 3.25 kcal mol^{-1}).[4a] Owing to the geminal substitution[2g,9] this interaction in *r*-2-*tert*-butyl-2,*cis*-6-dimethyl-1,3-oxathiane is likely to be slightly enhanced to, say, 14.6 kJ mol^{-1} (3.5 kcal mol^{-1}).

Now we are able to derive a value for $\Delta H^\circ_{\mathrm{CT}}$ from the experimental enthalpy difference (13.24 kJ mol^{-1} = 3.16 kcal mol^{-1}) between the epimeric 1,3-oxathianes (Table I), since $\Delta H^\circ_{\mathrm{exptl}} = [\Delta H^\circ_{\mathrm{CT}} + 2.64\ (0.63)] - 14.6\ (3.50)$ and $\Delta H^\circ_{\mathrm{CT}} = 13.24\ (3.16) - 2.64\ (0.63) + 14.6\ (3.50) = 25.2$ kJ mol^{-1} (6.0 kcal mol^{-1}). This estimate is not far from the gas-phase value, 22.5 kJ mol^{-1} (5.4 kcal mol^{-1}), based on appearance potential measurements.[5] Moreover, the latter value should in fact be revised upwards because of the double-buttressing effect in the reference chair form, 2,2,*cis*-4,6-dimethyl-1,3-oxathiane. In 2,2,*cis*-4,6-dimethyl-1,3-dioxane the magnitude of this effect is about 3.1 kJ mol^{-1} (0.74 kcal mol^{-1}).[2c,e,g] By comparing the corresponding interactions in 1,3-dioxanes[2b-e] and in 1,3-oxathianes[4,5] with each other the double-buttressing effect in 2,2,*cis*-4,6-dimethyl-1,3-oxathiane may be estimated at 2.5 kJ mol^{-1} (0.60 kcal mol^{-1}). Consequently, the corrected value of $\Delta H^\circ_{\mathrm{CT}}$ (g) is about 25 kJ mol^{-1} (6.0 kcal mol^{-1}).

1,3-Oxathiane itself has six possible twist conformations but only two possible chairs.[10] If all the twists are of the same energy, $\Delta S^\circ_{\mathrm{CT}}$ should be R ln 3 or 9.13 J mol^{-1} °K^{-1} (2.18 cal mol^{-1} °K^{-1}) and, accordingly, $\Delta G^\circ_{\mathrm{CT}}$ = 22.5 kJ mol^{-1} (5.4 kcal mol^{-1}). If any of the twist forms predominates, then $\Delta S^\circ_{\mathrm{CT}}$ will be somewhat smaller and $\Delta G^\circ_{\mathrm{CT}}$ somewhat higher. Thus we can estimate $\Delta G^\circ_{\mathrm{CT}}$ to be 23 ± 2 kJ mol^{-1} (5.5 ± 0.5 kcal mol^{-1}) at 298°K.

It may be of some interest to compare chair–twist energy differences in cyclohexane, 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane, and this has been done in Table II. The parameters presented for the 1,3-dithiane ring in ref 3 are suitable for 2,5-disubstituted derivatives only.[3] Other 1,3-dithianes[11] have clearly greater $\Delta H^\circ_{\mathrm{CT}}$ (16–20 kJ mol^{-1} or 4–5 kcal mol^{-1}) and $\Delta G^\circ_{\mathrm{CT}}$ (10–14 kJ mol^{-1} or 2.4–3.4 kcal mol^{-1}).

Experimental Section

r-2-*tert*-Butyl-2,*cis*-6-dimethyl-1,3-oxathiane was prepared earlier.[12] The equilibration method and the analysis of the equilibrium mixtures have been described before.[4]

Acknowledgments. The authors wish to thank the Finnish Cultural Foundation (P. P.), the Finnish Academy of Sciences (K. P.), The Royal Society (K. P.), the Science Research Council (K. P.), and the Finnish Academy, the Division of Sciences (K. P.), for support of this work.

Registry No.—*r*-2-*tert*-Butyl-2,*trans*-6-dimethyl-1,3-oxathiane, 51271-30-8; *r*-2-*tert*-butyl-2,*cis*-6-dimethyl-1,3-oxathiane, 51271-31-9.

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Rearrangements of α,β-Unsaturated α′-Halocyclobutanones

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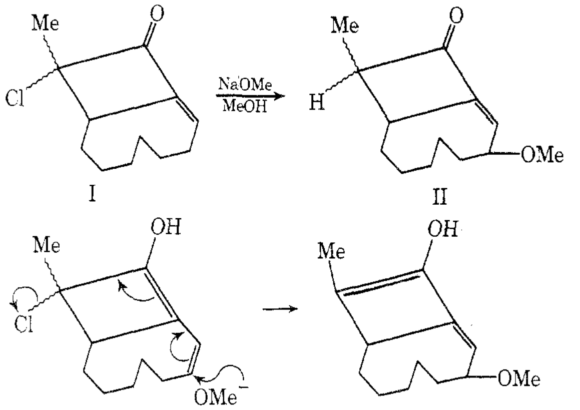
Received November 15, 1973

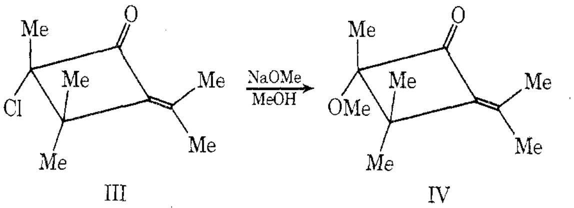
The base-catalyzed ring contraction of α-halocyclobutanones has been the subject of considerable study in recent years.[1] We have recently synthesized some α,β-unsaturated α′-halocyclobutanones[2] and now reveal the unexpected results obtained upon base treatment of such compounds.

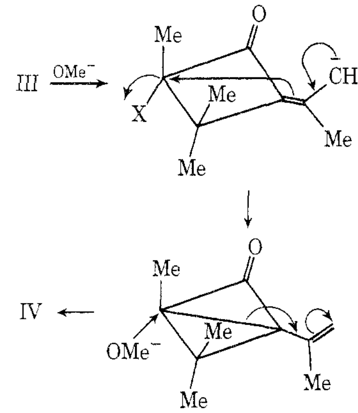
The treatment of 10-chloro-10-methylbicyclo[7.2.0]undec-1-en-11-one (I) with sodium methoxide in methanol resulted in allylic substitution rather than ring contraction to produce the 3-methoxy ketone II. The substitution



apparently occurs through the enol of the ketone. This substitution occurred readily at ambient temperature in an 80% yield.

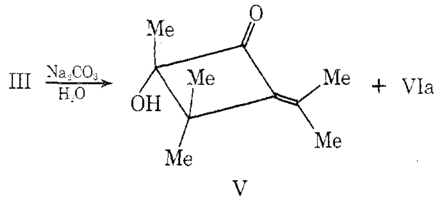
Conversely, the treatment of 2-chloro-4-isopropylidene-2,3,3-trimethylcyclobutanone (III) with sodium methoxide in methanol under identical conditions resulted in a direct substitution product, the 2-methoxy ketone IV, in 80% yield. Similarly, the methylbromo and ethylchloro compounds also give the direct substitution products. It seems unlikely that these substitution products are the result of a direct displacement because of the tertiary center. These products may result from an elimination proceeding through a bicyclobutanone intermediate which adds methoxide to furnish IV.[3] There is no evidence of ring contraction or any type of ring-opening reaction in any of these systems described.

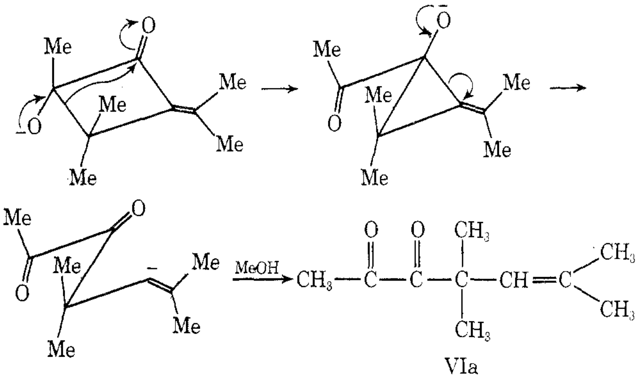




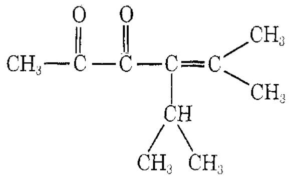
The different behavior of the two α,β-unsaturated α'-chlorocyclobutanones is intriquing. Perhaps the strain in the bicyclopropanone intermediate resulting from I is too severe for this pathway to be followed and the allylic substitution occurs instead.

Treatment of III with a 20% aqueous solution of sodium carbonate at reflux resulted in the expected hydroxy compound, V, and an unexpected product, VIa. The amount of VIa was dependent upon the reflux time and it soon became apparent that V was undergoing a ring-opening rearrangement reaction leading to VIa. The structure proposed for VIa is consistent with the elemental analysis, mass spectrum, infrared spectrum, and most significantly the nmr spectrum. This ring-opening reaction is believed to originate at the hydroxy group because the corresponding methoxy compound does not undergo this reaction. A mechanistic rationale is provided for the formation of this product.





The ring-contraction step is probably concerted from the alkoxide ion because the intermediate allylic carbanion should undergo a rapid proton transfer to yield VIb.

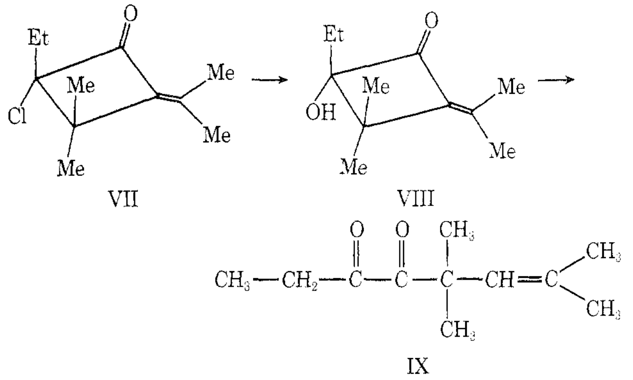


$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-\underset{CH(CH_3)_2}{\underset{|}{C}}=C(CH_3)_2$$

VIb

However, there was no evidence of an isopropyl group in the nmr spectrum, but a vinyl proton was apparent.

The hydrolysis of 2-chloro-2-ethyl-4-isopropylidene-3,3-dimethylcyclobutanone (VII) followed the same pathway, producing the hydroxy cyclobutanone VIII and the ring-opened dione IX.



In conclusion, α,β-unsaturated α'-chlorocyclobutanones undergo substitution reactions rather than ring contraction upon treatment with base. The α,β-unsaturated α'-hydroxyl compounds undergo an interesting ring-opening reaction to a dione.

Experimental Section

The unsaturated cyclobutanones, I, III, and VII were prepared by the *in situ* cycloaddition of methylchloro- and ethylchloroketenes with tetramethylallene and 1,2-cyclononadiene as previously described by us.[2]

General Procedure for Methoxy Substitution. A 5.0-g portion of the α,β-unsaturated α'-halocyclobutanone was treated with an excess of sodium methoxide in 50 ml of methanol. An immediate precipitate of sodium chloride was observed at room temperature.

After the addition of 100 ml of water the reaction solution was extracted with chloroform. The chloroform extracts were dried and rotoevaporated. The residue was distilled under reduced pressure.

3-Methoxy-10-methylbicyclo[7.2.0]undec-1-en-11-one (II). The methoxy substitution product was distilled at 83–85° (0.005 mm): yield 80%; ir 1760 (C=O) and 1660 cm^{-1} (C=C); nmr δ 1.2 (d, 3 H), 1.5 (m, 11 H), 3.2 (s, 3 H), 3.4 (m, 1 H), and 5.6 (m, 2 H).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 75.00; H, 9.62. Found: C, 74.68; H, 9.58.

4-Isopropylidene-2-methoxy-2,3,3-trimethylcyclobutanone (IV). This methoxy substitution product was isolated in 80% yield at 60° (0.5 mm): ir 1760 (C=O) and 1660 cm^{-1} (C=C); nmr δ 1.20 (s, 3 H), 1.22 (s, 3 H), 1.24 (s, 3 H), 1.8 (s, 3 H), 2.02 (s, 3 H), and 3.4 (s, 3 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.53; H, 9.89. Found: C, 72.09; H, 10.00.

This methoxy substitution product was also obtained from the corresponding bromocyclobutanone.

Hydrolysis of 2-Chloro-4-isopropylidene-2,3,3-trimethylcyclobutanone (III). 2-Hydroxy-4-isopropylidene-2,3,3-trimethylcyclobutanone (V) and 4,4,6-Trimethyl-5-heptene-2,3-dione (VI). A 10-g portion of III was treated with 100 ml of 20% aqueous sodium carbonate at reflux with stirring for 20 hr. Upon cooling, the reaction mixture was extracted with chloroform and the extracts were dried over anhydrous calcium chloride. The solvent was removed by rotoevaporation and the residue was vacuum distilled. Two major fractions were obtained.

(1) The first fraction (VI) was a deep yellow colored liquid at 38–40° (0.8 mm): ir 1710 (C=O) and 1650 cm^{-1} (C=C); nmr δ 1.3 (s, 6 H), 1.5 (s, 3 H), 1.7 (s, 3 H), 2.24 (s, 3 H), and 5.3 (s, 1 H); mass spectrum parent peak at *m/e* 168 (theory 168) and major peaks at *m/e* 97 and 125 due to the loss of $CH_3C{=}O$ and $(H_3C({=}O)C{=}O$ and another at *m/e* 55 which is due to $-CH{=}C(CH_3)_2$.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.42; H, 9.52. Found: C, 71.59; H, 9.82.

(2) The second fraction (V) distilled at 85° (0.08 mm): ir 3400 (OH), 1740 (C=O), and 1660 cm^{-1} (C=C); nmr δ 1.3 (s, 6 H), 1.4 (s, 3 H), 1.9 (s, 3 H), 2.15 (s, 3 H), and 4.4 (s, 1 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.42; H, 9.52. Found: C, 71.12; H, 9.38.

The total yield was 80% but the distribution of V and VIa was very dependent upon the reaction time. Under the conditions described, the distribution was a 20% yield of VIa and a 60% yield of V.

Hydrolysis of V. The hydroxy compound upon treatment with aqueous sodium carbonate as described above was converted to the yellow liquid, VIa.

Hydrolysis of 2-Chloro-2-ethyl-4-isopropylidene-3,3-dimethylcyclobutanone (VII). 2-Ethyl-2-hydroxy-4-isopropylidene-3,3-dimethylcyclobutanone (VIII) and 5,5,7-Trimethyl-6-octene-3,4-dione (IX). The same procedure was employed as described above. Two fractions were obtained as follows.

(1) The first fraction (IX) was a deep yellow colored liquid at 50° (0.15 mm): ir 1710 (C=O) and 1650 cm^{-1} (C=C); nmr δ 1.0 (t, 3 H), 1.3 (s, 6 H), 1.5 (s, 3 H), 1.7 (s, 3 H), 2.6 (q, 2 H), and 5.3 (s, 1 H); mass spectrum parent peak at *m/e* 182 (theory 182), with major peaks at *m/e* 97 and 125 due to loss of $CH_3CH_2C{=}O$ and $CH_3CH_2C({=}O)C{=}O$ and also at *m/e* 55 and 57 due to $-CH{=}C(CH_3)_2$ and $CH_3CH_2C{=}O$.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 9.8. Found: C, 72.37; H, 9.92.

(2) The second fraction (VIII) was collected at 90–92° (0.08 mm): ir 3400 (OH), 1740 (C=O), and 1660 cm^{-1} (C=C); nmr δ 1.0 (t, 3 H), 1.28 (s, 3 H), 1.36 (s, 3 H), 1.6 (q, 2 H), 1.84 (s, 3 H), 2.05 (s, 3 H), and 4.15 (s, 1 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 9.8. Found: C, 72.23; H, 9.78.

Acknowledgments. The authors wish to express appreciation to the Robert A. Welch Foundation and the North Texas State University Faculty Research Fund for support of this investigation.

Registry No.—I, 42915-23-1; II, 51270-76-9; III, 42915-13-9; IV, 51270-77-0; V, 51270-78-1; VIa, 51270-79-2; VII, 42915-15-1; VIII, 51270-80-5; IX, 51270-81-6; 2-bromo-4-isopropylidene-2,3,3-trimethylcyclobutane, 42915-14-0.

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(3) The methoxide ion could attack the unsymmetrical bicyclobutanone at either bridgehead carbon, but attack at the one indicated produces a significantly more stable carbanion.

2,5-Dicarbomethoxy-3,4-diphenylcyclopentadienone. Synthesis and Reaction with Acetylenes

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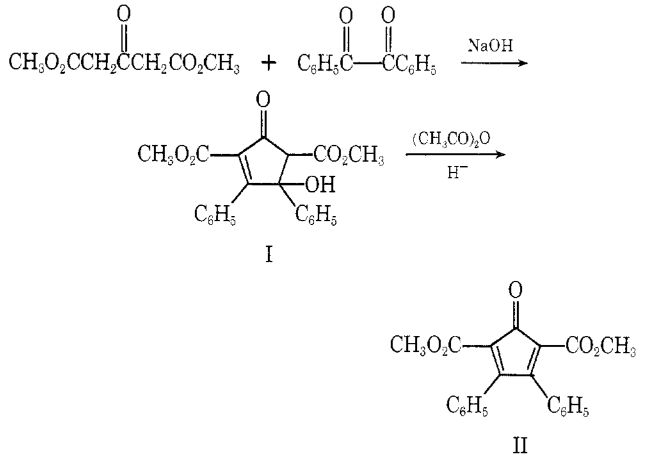
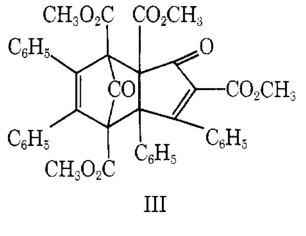
Received December 20, 1973

Diels-Alder additions of cyclopentadienones to acetylenes offer a convenient route to arenes.[1,2] If the cyclopentadienones contained functional groups which did not interfere with the addition reaction, useful functionality could be introduced into the products. We have found that 2,5-dicarbomethoxy-3,4-diphenylcyclopentadienone (II) does react with acetylenes to form the desired arene diesters. Compound II can be readily synthesized from available starting materials. It differs from most diphenylcyclopentadienones[1] in that at 25° it is predominantly monomeric in solution and only partially dimerized in the solid state. The synthesis and some properties of II are described below.

Base-catalyzed condensation of dimethyl acetonedicarboxylate with benzil produced the cyclopentenolone I, which appeared to be partially enolized in solution based on the nmr spectrum. Acid-catalyzed dehydration with acetic anhydride produced II, a bright-orange solid. Compound II is primarily a monomer, as shown by the strong methyl resonance in the ^1H nmr at δ 3.75. Four weak resonances of equal intensity at δ 3.38, 3.51, 3.81, and 3.83 correspond to the methyl resonances expected for III and indicate a molar ratio of II to III of *ca.* 30:1. The ^{13}C nmr





III