carbonate. The solvent was removed under vacuum and gave no evidence of the presence of ketone **5** as confirmed by the ir spectrum (no C=O absorption at 1705 cm^{-1}), and nmr (CCl_4) showed no benzyl hydrogen at τ 6.60.

Registry No.—**1**, 29478-03-3; **2**, 29478-04-4; **3**, 29478-05-5; **3** 2,4-DNP, 29478-06-6; **5**, 29478-07-7; **6**, 29478-08-8; *N*-bromosuccinimide, 128-08-5.

Halogenated Ketenes. XX. Substitution *vs.* Rearrangement of Halogenated Ketene Olefin Cycloadducts[1,2]

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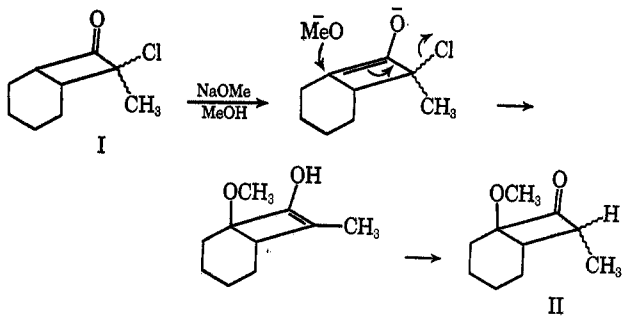
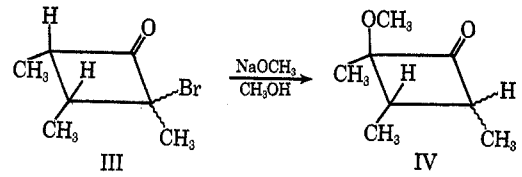
Two communications have recently appeared which describe a base-catalyzed rearrangement of a cycloadduct of a halogenated ketene and an olefin leading to a bifunctional cyclopropane.[3,4] These reports prompt us to describe our results on the rearrangement of a bicyclo[3.2.0]hept-2-en-6-one ring system to the bicyclo[3.1.0]hex-2-ene ring system in the presence of sodium methoxide in refluxing methanol. This ring system undergoes rearrangement in contrast to other systems studied by us and other workers which undergo substitution under similar conditions.

Fletcher and Hassner have reported that the dichloroketene adducts of cholestene and cyclohexene undergo rearrangement under the influence of methoxide to produce 1-methoxy-7-carbomethoxybicyclo[4.1.0]-heptane in the latter case and the corresponding rearranged product in the former. A proposed mechanism involves enolization, followed by methoxy substitution on C_6 (this intermediate was isolated) and subsequent loss of the second chlorine atom and rearrangement to the bicyclo[4.1.0]heptane derivative.

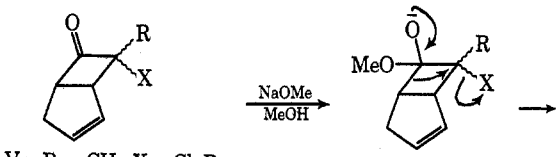
When the adduct of methylchloroketene and cyclohexene (I) was treated with a threefold excess of sodium methoxide in refluxing methanol, II was obtained in approximately 60% yield as the only volatile product. This compound corresponds to Hassner's intermediate, except that in this case a second leaving group is not



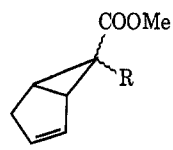


available for further rearrangement. Similarly, when the adduct of methylbromoketene and *cis*-2-butene (III) was treated with methoxide, the substitution product (IV) was obtained in 70% yield.

However, when the methylchloro- or methylbromoketene adduct of cyclopentadiene (V) was heated with



Va, R = CH_3; X = Cl, Br
b, R = H; X = Cl, F
c, R = vinyl; X = Br

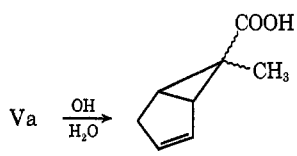


VIa, R = CH_3
b, R = H
c, R = vinyl

sodium methoxide in methanol, rearrangement occurred rather than substitution. The methoxide ion attacks the carbonyl carbon atom, thus leading to the rearranged product (VI). This is consistent with the mechanism proposed by Brook, *et al.*, and is formally analogous to the Favorski rearrangement of α-haloketones.[4,5] This rearrangement was observed with several halogenated ketene–cyclopentadiene adducts as illustrated.

The structure of VI was established by elemental analysis, infrared spectra and the following nmr and and mass spectral data. The chemical shift of the bridgehead protons in the nmr spectra of VI ranged from δ 1.0 to 2.5, and the corresponding bridgehead protons in the bicyclo[3.2.0]hept-2-en-6-ones appear at δ 3.5–4.3;[6] the chemical shift of the ester methoxy protons occurred at a position characteristic of an ester (δ 3.5–3.7) rather than at a position characteristic of an ether (δ 3.2–3.3). A parent peak at *m/e* 152 for VIa was observed in the mass spectrum; a very intense peak was also observed at *m/e* 93 resulting from the loss of a carbomethoxy group.

As a further verification of the structure of VIa, Va was treated with 20% aqueous sodium hydroxide solution, resulting in the formation of a carboxylic acid (VII). This acid was converted to the methyl ester by treatment with thionyl chloride and then methanol.



(1) Paper XIX: W. T. Brady and J. P. Hieble, *Tetrahedron Lett.*, 3205 (1970).

(2) Support of this investigation by The Robert A. Welch Foundation, National Science Foundation (GP-14016), and a North Texas State University Faculty Research Grant is gratefully acknowledged.

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(4) P. R. Brook, J. M. Harrison, and A. J. Duke, *Chem. Commun.*, 589 (1970).

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The ester produced in this manner was identical with VIa as evidenced by nmr, ir, and mass spectra.

In the rearrangement reactions of V, the rearranged products (VI) were the only products isolated from the reaction mixtures. There was considerable polymer and tar formation in some of the systems resulting in a low yield of rearranged product. There was some indication of trace amounts of the product resulting from methoxy substitution on C_5; however, there was no evidence for direct methoxy substitution on C_7.

The adducts of nonhalogenated ketenes and cyclopentadiene (either aldoketene or ketoketene adducts) were inert to the reaction conditions used to produce the above rearrangements. However, some isomerization was observed in the aldoketene adducts.

The tendency for cyclopentadiene adducts to undergo rearrangement, to the exclusion of substitution on C_5, can be explained by considering the stability of the enol formed by the loss of the bridgehead hydrogen adjacent to the carbonyl. This enol must be formed to account for substitution at this carbon. It is obvious that this enol would be more stable in the *cis*-2-butene and cyclohexene adducts than in the adducts of cyclopentadiene, owing to the increased amount of strain in the latter system because of the double bond on the bridgehead carbon.

Therefore, the treatment of halogenated ketene–olefin cycloadducts with sodium methoxide results in substitution. This substitution is dependent on enolization and, when the enolization is retarded, a Favorski-type rearrangement occurs.

Experimental Section

We have previously described the preparation of the following cycloadducts: methylchloro- and methylbromoketene–cyclopentadiene (Va),[6] chloro- and fluoroketene–cyclopentadiene (Vb),[7] and methylchloroketene–cyclohexene (I).[8] 2,3-Dibromobutanoyl chloride was obtained by the bromination of crotonic acid and subsequent reaction with thionyl chloride.

2-Bromo-2,3,4-trimethylcyclobutanone (III).—A 20-g (0.12 mol) portion of 2-bromopropanoyl chloride was added dropwise with vigorous stirring to a solution of 25 ml (0.2 mol) of triethylamine and 80 ml (1 mol) of *cis*-2-butene in 200 ml of dry hexane at 0°. The reaction flask was fitted with a cold-finger condenser filled with Dry Ice–acetone to prevent loss of *cis*-2-butene. The reaction mixture was allowed to stand for 3 hr and then the amine salt was removed by filtration. Concentration on a rotatory evaporator and distillation afforded 5 g (22%): bp 40–42° (0.1 mm); ir 1800 cm^{-1}; nmr (CCl_4) (both isomers) δ 1.1 (d, 6 H, J = 8 Hz), 1.68 and 1.87 (two s, 3 H), 2.48 (m, 1 H), and 3.45 (m, 1 H).

Anal. Calcd for $C_7H_{11}BrO$: C, 43.9; H, 5.75. Found: C, 43.83; H, 5.50.

7-Bromo-7-vinylbicyclo[3.2.0]hept-2-en-6-one (Vc).—A 66-g (0.25 mol) portion of 2,3-dibromobutanoyl chloride was added dropwise with vigorous stirring to a solution of 35 ml (0.25 mol) of triethylamine and 80 ml (1 mol) of cyclopentadiene in 200 ml of dry hexane at 0–5°. This mixture was stirred overnight and then filtered to remove the amine salt. The filtrate was concentrated on a rotatory evaporator and distilled. The cycloadduct initially formed dehydrobrominated readily and, after three distillations, the vinylbromoketene–cyclopentadiene adduct was obtained: bp 80–82° (1 mm); ir 1800 and 1650 cm^{-1}; nmr (CCl_4) δ 2.7 (m, 2 H), 4.0 (m, 2 H), and 5.6 (m, 5 H).

Anal. Calcd for C_9H_9BrO: C, 50.73; H, 4.26. Found: C, 50.43; H, 4.61.

General Procedure for Sodium Methoxide Treatment of Cycloadducts.—A 150-ml portion of methanol to which 4 g of sodium had been added was vigorously refluxed while a solution of 10 g of the ketene–olefin cycloadduct in 25 ml of methanol was added. There was an immediate precipitation of the sodium halide with all of the halogenated ketene adducts. Refluxing was continued for 15 min and then the mixture was added to 150 ml of water. This aqueous mixture was extracted with chloroform. After the combined extracts were dried, the solvent was removed on a rotatory evaporator and the residue was distilled to yield the product.

8-Methyl-6-methoxybicyclo[4.2.0]octan-7-one (II).—A 60% yield was obtained: bp 56–58° (1.8 mm); ir 1780 cm^{-1}; nmr (CCl_4) δ 1.15 (d, 3 H, J = 8 Hz), 1.8 (m, 10 H), and 3.45 (s, 3 H).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.3; H, 9.52; mol wt, 168. Found: C, 70.5; H, 9.17; mol wt (mass spectrum), 168.

2-Methoxy-2,3,4-trimethylcyclobutanone (IV).—A 70% yield was obtained: bp 98–100° (60 mm); ir 1780 cm^{-1}; nmr (CCl_4) δ 1.2 (m, 9 H), 2.1 (m, 2 H), and 3.2 (s, 3 H).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.50; H, 9.85. Found: C, 67.14; H, 9.78.

***endo*-6-Carbomethoxy-*exo*-6-methylbicyclo[3.1.0]hex-2-ene (VIa).**—About a 60% yield was obtained from either the methylchloroketene–cyclopentadiene adduct or the methylbromoketene–cyclopentadiene adduct: bp 60–62° (2 mm); ir 1740 cm^{-1}; nmr (CCl_4) δ 1.3 (s, 3 H), 1.6 (m, 1 H), 2.0 (m, 1 H), 2.6 (m, 2 H), 3.55 (s, 3 H), and 5.52 (m, 2 H); mass spectrum parent peak at 152 (theory 152), major peak at 93 (VIa − carbomethoxy).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.0; H, 7.9. Found: C, 70.97; H, 8.26.

6-Carbomethoxybicyclo[3.1.0]hex-2-ene (VIb).—A 15% yield was obtained from the chloroketene–cyclopentadiene adduct and a 10% yield from the corresponding fluoroketene adduct: bp 55° (2.5 mm); ir 1730 cm^{-1}; nmr (CCl_4) (both isomers) δ 2.3 (complex m, 5 H), 3.58 and 3.7 (two s, 3 H), and 5.7 (m, 2 H).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.5; H, 7.25. Found: C, 69.49; H, 7.52.

6-Carbomethoxy-6-vinylbicyclo[3.1.0]hex-2-ene (VIc).—A 15% yield was obtained: bp 70–72° (2.5 mm); ir 1730 and 1630 cm^{-1}; nmr (CCl_4) (both isomers) δ 2.4 (m, 5 H), 3.58 and 3.64 (2 s, C H), and 5.4 (m, 5 H).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.1; H, 7.31. Found: C, 72.6; H, 7.89.

6-Carboxy-6-methylbicyclo[3.1.0]hex-2-ene (VII).—A 10-g (0.06 mol) portion of Va was added to 200 ml of 20% aqueous NaOH solution and the resulting mixture was refluxed for 16 hr. After the mixture was cooled and acidified with dilute HCl solution, the product was extracted into chloroform. The combined extracts were dried and concentrated on a rotatory evaporator. Distillation afforded 5 g (60%) of VII: bp 100–102° (0.2 mm); mp 40–45° (solidification occurred in the receiver); nmr (CCl_4) δ 1.05 and 1.4 (2 s, 3 H), 2.6 (m, 4 H), 5.7 (m, 2 H), and 11.8 (s, 1 H).

Anal. Calcd for $C_8H_{10}O_2$: C, 69.6; H, 7.25. Found: C, 69.81; H, 7.50.

Registry No.—II, 29494-54-0; III, 29478-01-1; IV, 29478-02-2; Vc, 29494-55-1; VIa, 29494-56-2; VIb, 29494-57-3; VIc, 29494-58-4; VII, 29494-59-5.

(7) W. T. Brady and E. F. Hoff, Jr., *J. Amer. Chem. Soc.*, **90**, 6256 (1968).
(8) W. T. Brady and R. Roe, Jr., *ibid.*, **93**, 1662 (1971).