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HALOGENATED KETENES—IV

CYCLOADDITIONS OF ALKYLHALOKETENES[1,2]

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Abstract—Methylbromo, ethylbromo- and ethylchloroketenes have been prepared and undergo 1,2-cycloaddition with cyclopentadiene to form bicyclo[3.2.0]hept-2-en-6-ones. The cycloadducts were prepared by generating the alkylhaloketenes by dehydrohalogenation of the appropriately substituted acid halide in the presence of cyclopentadiene. Methylchloroketene also undergoes cycloaddition very readily with ethyl vinyl ether. *cis* and *trans* Isomers were produced in all cases and the isomer distributions determined.

REGARDING reports on the preparation of some alkylhaloketenes, ethylchloro-, methylbromo- and ethylbromoketenes polymerize very rapidly.[5–7] Consequently, in an effort to obtain cycloadducts of alkylhaloketenes, the latter were prepared by dehydrohalogenation of the appropriately substituted acid halide in the presence of olefinic compounds. Recently, the preparation and cyclo-addition of methylchloroketene with cyclopentadiene by this method was reported.[2] This paper describes the cycloaddition of several other alkylhaloketenes with cyclopentadiene and methylchloroketene with ethyl vinyl ether. Unlike the dihaloketenes, dichloroketene[8] and dibromoketene,[9] the alkylhaloketenes are unsymmetrical and yield *cis* and *trans* isomers upon cycloaddition. These ketenes undergo 1,2-cycloadditions with

cis

trans

cyclopentadiene to give *cis* and *trans* substituted bicyclo[3.2.0]hept-2-en-6-ones, according to the following general equation. The structures of the cycloadducts were proved by a combination of elemental analysis and IR and NMR spectra. The cyclobutanone structure was assigned to the adduct in preference to the following

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[2] Paper III. W. T. Brady and B. M. Holifield, *Tetrahedron Letters* No. 45, 5511 (1966).

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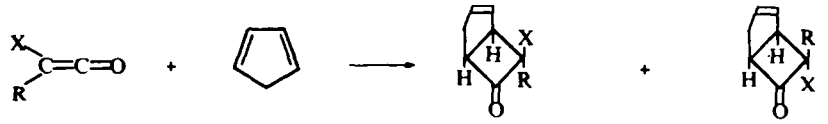
[5] H. Staudinger, E. Anthes and H. Schneider, *Ber. Dtsch. Chem. Ges.* **46**, 3539 (1913).

[6] E. Ott, *Liebigs Ann.* **401**, 159 (1914).

[7] H. Staudinger and H. Schneider, *Helv. Chim. Acta* **6**, 304 (1923).

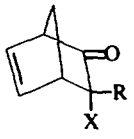
[8] W. T. Brady, H. G. Liddell and W. L. Vaughn, *J. Org. Chem.* **31**, 626 (1966).

[9] W. T. Brady, *J. Org. Chem.* **31**, 2676 (1966).

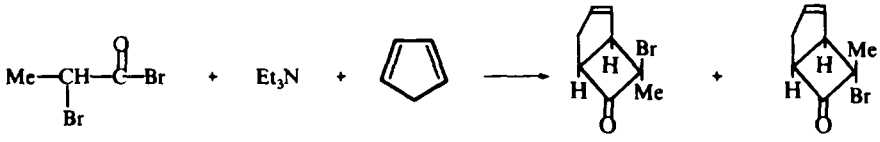


trans *cis*

Diels-Alder adduct on the basis of the characteristic IR adsorption band of 1800 cm^{-1} for cyclobutanones.[10–12] The double bond location was assigned on the basis that the diene acts as a nucleophile which would be expected to yield the above substituted cyclobutanone regardless of whether an ionic process or diradical mechanism was operative.[13] Also, this is compatible with the orientation of the cycloadduct of cyclopentadiene and ketene,[14] dimethylketene,[15] dichloroketene[16] and diphenylketene.[17]



Methylbromoketene, prepared by the dehydrobromination of α-bromopropionyl bromide, reacted with cyclopentadiene *in situ* at 0–5° to give 7-bromo-7-methylbicyclo[3.2.0]hept-2-en-6-one in 30% yield. The isomer distribution was 2:1 as



determined by VPC. The structure of the cycloadduct was proved by a combination of elemental analysis and IR and NMR spectra. The two isomers were separated by careful fractionation. The structure of the *cis* and *trans* isomers were established by NMR. In the communication regarding the cycloaddition of methylchloroketene and cyclopentadiene, it was established that the chemical shift of the Me group of the *cis* isomer is shifted upfield because of shielding by the double bond. This is also the case for the *cis* isomer of the cycloadduct of methylbromoketene and cyclopentadiene. One isomer had a Me singlet at 1·9 ppm and the other isomer a Me singlet at 1·6 ppm. When each isomer in chloroform was treated with bromine, the NMR spectrum of the isomer with the singlet at 1·9 ppm was unchanged. However, the spectrum of the other isomer was altered. The singlet at 1·6 ppm had greatly diminished and there was a new singlet at 1·9 ppm. This is interpreted to mean that the Me group

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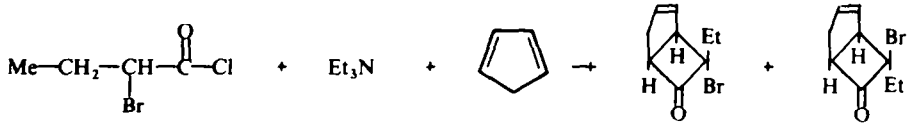
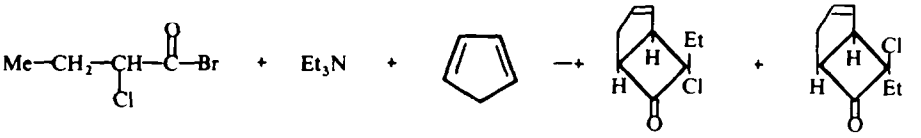
[11] F. V. Brutcher, Jr., T. Roberts, S. J. Barr and N. Pearson, *J. Am. Chem. Soc.* **78**, 1507 (1956).
[12] J. C. Martin, P. G. Gott, V. W. Goodlett and R. H. Hasek, *J. Org. Chem.* **30**, 4175 (1965).
[13] J. D. Roberts and C. M. Sharts, *Organic Reactions* Vol. 12; p. 26 (1962).
[14] [a] B. T. Brooks and G. Wilbert, *J. Am. Chem. Soc.* **63**, 870 (1941); [b] J. D. Robertson and W. F. Gorham, *Ibid.* **74**, 2278 (1952).
[15] T. L. Dawson and G. R. Ramage, *J. Chem. Soc.* 3523 (1950).
[16] H. C. Stevens, D. A. Reich, D. R. Brandt, K. R. Fountain and E. J. Gaughan, *J. Am. Chem. Soc.* **87**, 5257 (1965).
[17] J. R. Lewis, G. R. Ramage, J. L. Simonsen and W. G. Wainwright, *J. Chem. Soc.* 1837 (1937).

of the *cis* isomer is shifted upfield because it falls into the shielding cone associated with the π-electron system of the double bond. Consequently, the isomer distribution of 2:1 was *trans* to *cis*.

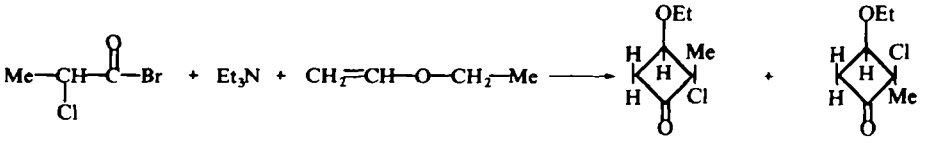
Ethylbromoketene, prepared by the dehydrochlorination of α-bromobutyryl chloride, underwent cycloaddition with cyclopentadiene to yield a mixture of isomers of 7-bromo-7-ethylbicyclo[3.2.0]hept-2-en-6-one in 66% yield. The isomer distribution was 1:1 as evidence by VPC.



Ethylchloroketene, prepared by the dehydrobromination of α-chlorobutyryl bromide, reacted *in situ* with cyclopentadiene to yield 7-chloro-7-ethylbicyclo[3.2.0]-hept-2-en-6-one in 39% yield. The isomer distribution was found to be 4:1 by VPC.



In the cycloaddition of methylchloroketene and cyclopentadiene the isomer distribution of *cis* to *trans* was 3:1. The cycloaddition of methylchloroketene and ethyl vinyl ether has been accomplished and the isomer distribution was found to be 3:1. This cycloadduct was prepared as illustrated by the following equation:



It is possible that the isomer distribution determined from the reaction mixtures represents some equilibrium distribution. To establish that this was not the case and that isomerization was not occurring, a control experiment was run. The cycloadduct of ethylbromoketene and cyclopentadiene (80% *cis* and 20% *trans*) was added to a synthetic mixture which approximated the conditions of preparation of the cycloadduct. It was found that there was no change in the isomer distribution of 4:1. Consequently, the isomer distribution as determined by VPC of the reaction solution must represent the actual isomer distribution formed and not some equilibrium mixture of isomers.

DISCUSSION

This investigation indicates that alkylhaloketenes can be successfully prepared by the dehydrohalogenation of the appropriately substituted acid halide. Furthermore, these ketenes enter into cycloadditions readily with reactive olefins. Methylchloroketene and the alkylhaloketenes reported in this paper are not immediately polymerized in the presence of the amine salt and can be isolated in solution for subsequent work. This is in contrast to the earlier work whereby ethylchloro-, methylbromo- and

ethylbromoketenes polymerized very rapidly when prepared by the thermal decomposition of appropriately substituted malonic anhydrides. In the cycloadditions reported here, undoubtedly the undesirable polymerization of these labile ketenes in the presence of the amine salts is a competing reaction which decreases the yields of cycloadducts.

The isomer distributions of the cycloadducts formed with cyclopentadiene are very surprising. Particularly, the reversal in distribution of the methylchloroketene cyclopentadiene adduct (3:1 *cis* to *trans*) and the methylbromoketene cyclopentadiene adduct (2:1 *trans* to *cis*). It would seem that this could possibly be due to an interaction between the bromine atom and the unsaturated system. A molecular model indicates that the bromine atom is right over this π-electron system. Possibly bromine has an orbital far enough out to interact appreciably with this unsaturated system, whereas chlorine does not. Perhaps this interaction occurs in the transition state and causes the *trans* isomer to predominate.

It certainly appears that the orientation of unsymmetrical ketenes to cyclopentadiene is not determined solely by steric interactions. An interaction as described above with the π-electron system might just influence the isomer distribution in all cases. At any rate a more extensive investigation of the cycloadditions of alkylhaloketenes is in progress in an effort to determine the nature of this process and also explain the isomer distributions reported above.

EXPERIMENTAL

α-Chloropropionic acid, α-chlorobutyric acid, α-bromopropionic acid and α-bromobutyric acid were commercially available. α-Chloropropionyl bromide, α-bromopropionyl bromide and α-chlorobutyryl bromide were all prepared from the appropriate acid and PBr_3. α-Bromobutyryl chloride was prepared from the corresponding acid and $SOCl_2$. Mol. wts. were obtained on a Mechrolab 301A vapor pressure osmometer. NMR spectra were recorded on a Varian A-60 instrument at 60 Mc with TMS as an internal standard.

7-Bromo-7-methylbicyclo[3.2.0]*hept-2-en-6-one.* To a mixture of 22 g (0·218 mole) EtN_3, 120 g (1·82 mole) cyclopentadiene and 100 ml dry hexane at 0–5°, 39·3 g (0·182 mole) α-bromopropionyl bromide in 25 ml hexane was added dropwise over a 30 min period under a N_2 atm. After the addition was complete, the mixture was stirred an additional hr while warming to room temp. The Et_3NHBr which precipitated from the reaction soln during the addition was removed by filtration and washed with hexane. There was obtained a theoretical amount of salt. The hexane soln was concentrated on a steam bath and vacuum distilled. There was obtained 11 g of crude product which corresponds to a 30% yield. This material was carefully fractionated through a 6" vigreaux column and the two isomers were found to be present at 89–91° and 96–97° at 5 mm. Analysis by VPC of the reaction soln showed an isomer distribution of 2:1. IR absorption of both isomers: 1800 cm^{-1} (s) and 1605 cm^{-1} (w); NMR spectrum ($CHCl_3$) for higher boiling *trans* isomer: multiplets were centered at 5·8 ppm (vinyl protons); at 3·8 ppm (methinyl protons), and at 2·6 ppm (methylene protons); singlets at 1·9 ppm (Me protons) and at 1·6 ppm (Me protons of *cis* isomer (12%)). The area ratios of these peaks (excluding the one at 1·6 ppm) were 2:2:2:3; NMR spectrum ($CHCl_3$) for low boiling *cis* isomer: multiplets were centered at 5·8 ppm (vinyl protons), at 4·4 ppm (methinyl proton), at 3·9 ppm (methinyl proton), and at 2·6 ppm (methylene protons), singlets at 1·9 ppm (Me protons of *trans* isomers (10%)), and at 1·6 ppm (Me protons). These peak areas (excluding the one at 1·9 ppm) were in the ratio of 2:1:1:2:3. (Found: C, 47·90; H, 4·56; mol. wt. 213. Calc. for C_8H_9BrO: C, 47·76; H, 4·48%; mol. wt. 201.)

7-Bromo-7-ethylbicyclo[3.2.0]*hept-2-en-6-one.* A soln of 31·2 g (0·168 mole) α-bromobutyryl chloride in 25 ml hexane was added to a soln of 20·4 g (0·202 mole) Et_3N, 111 g (1·68 mole) cyclopentadiene and 100 ml dry hexane at 0–5° under a N_2 atm. There was obtained 23·9 g (66%) of crude cycloadduct. Careful fractionation afforded the two isomers at 107–108° and 111–114° at 5 mm. Analysis by VPC of the reaction soln indicated an isomer distribution of 1:1. IR absorption: 1800 cm^{-1} (s) and 1605 cm^{-1} (w); NMR

spectrum ($CHCl_3$) of both isomers: multiplets were centered at 5·8 ppm (vinyl protons), at 3·8 ppm (methinyl protons), at 2·6 ppm (methylene protons on ring), at 1·9 ppm (methylene protons of ethyl group) and at 1·1 ppm (Me protons). The area ratios of these peaks were 2:2:2:2:3. (Found: C, 50·46; H, 5·31; mol. wt. 224. Calc. for $C_9H_{11}BrO$: C, 50·23; H, 5·12%; mol. wt. 215.)

7-Chloro-7-ethylbicyclo[3.2.0]hept-2-en-6-one. A soln of 24·2 g (0·24 mole) Et_3N, 122 g (2 moles) cyclopentadiene and 100 ml dry hexane was cooled to 0–5° under a N_2 atm. α-Chlorobutyryl bromide (0·2 mole) in 25 ml hexane was added dropwise to this cold soln. There was obtained 13·5 g (39%) of crude cycloadduct. Careful fractionation yielded the two isomers at 88–90° and 93–94° at 5 mm. Analysis by VPC of the reaction soln showed an isomer distribution of 4:1. IR absorption: 1800 cm^{-1} (s) and 1605 cm^{-1} (w): NMR spectrum ($CHCl_3$) of both isomers: multiplets were centered at 5·8 (vinyl protons), at 3·8 (methinyl protons), at 2·6 (methylene protons of ring), at 1·8 (methylene protons of Et group) and at 1·1 (Me protons). The area ratios of these peaks were 2:2:2:2:3. (Found: C, 63·89; H, 6·73; mol. wt. 179. Calc. from $C_9H_{11}ClO$: C, 63·53; H, 6·47%; mol. wt. 170.)

2-Chloro-2-methyl-3-ethoxycyclobutanone. A 43 g (0·25 mole) portion of α-chloropropionyl bromide in 25 ml hexane was added dropwise to a soln of 30 g (0·30 mole) Et_3N, 90 g (1·25 mole) ethyl vinyl ether and 100 ml dry hexane at 0–5° under a N_2 atm. There was obtained 20 g (50%) of the cycloadduct. Analysis by VPC of the reaction soln showed an isomer distribution of 3:1. Careful fractionation of the adduct yielded a fraction at 63–65° and a second fraction at 71–73° at 2 mm. IR absorption: 1800 cm^{-1} (s) and 1050–1150 (s); NMR spectrum ($CHCl_3$) of both isomers: triplet at 4·3 (methinyl proton), quartet at 3·6 (methylene protons of ethoxy), multiplet centered at 3·2 (methylene protons on ring), singlet at 1·6 (Me protons on ring) and triplet at 1·25 (Me protons of ethoxy). The area ratios of these peaks were 1:2:2:3:3. (Found: C, 51·4; H, 6·97. Calc. for $C_7H_{11}ClO_2$: C, 51·7; H, 6·83%.)

Attempted isomerization of 7-bromo-7-ethylbicyclo[3.2.0]hept-2-en-6-one. A 1·0 g portion of 7-bromo-7-ethylbicyclo[3.2.0]hept-2-en-6-one (80% low boiling isomer and 20% high boiling isomer as determined by VPC) was dissolved in 10 ml dry hexane. To this soln was added a few drops of Et_3N, 4 g Et_3NHCl and 10 ml cyclopentadiene. This mixture was cooled to 0–5° and stirred for 2 hr. The isomer distribution of the cycloadduct of ethylbromoketene and cyclopentadiene was checked by VPC at intervals of ½, 1 and 2 hr. There was no change in the distribution as it remained constant at 4:1.

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