6137-03-7; pinacolone, 75-97-8; 4-methyl-2-pentanone, 108-10-1; 4,4-dimethyl-2-pentanone, 590-50-1.

Acknowledgments.—The authors wish to express their gratitude to Professor Arne Fredga for all facilities placed at their disposal. The research was supported by the Swedish Natural Science Research Council.

Halogenated Ketenes. V. Cycloadditions of Dichloroketene to Olefins[1]

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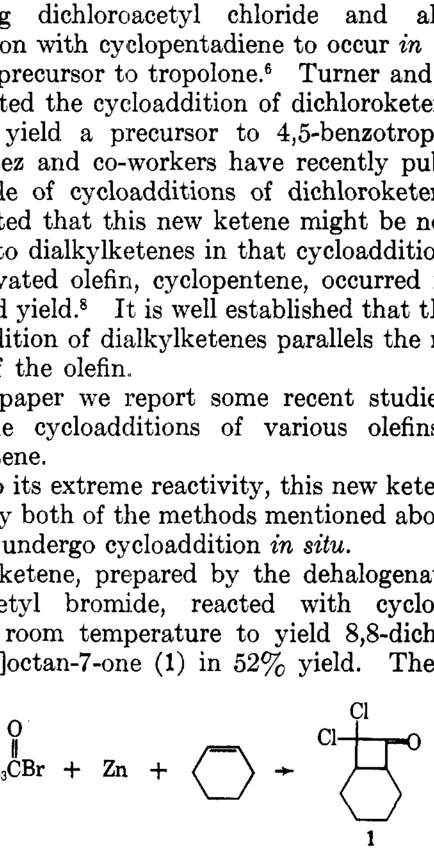
Received April 28, 1967

There have been several reports from this laboratory recently on the preparation and characterization of some new halogenated ketenes.[2–5] There appears to be a considerable amount of interest in these new reactive materials and in dichloroketene cycloadditions in particular. One of us has previously reported the preparation of this ketene by the dehalogenation of trichloroacetyl bromide with activated zinc.[2] Stevens and co-workers also prepared it by dehydrochlorinating dichloroacetyl chloride and allowing cycloaddition with cyclopentadiene to occur *in situ* to produce a precursor to tropolone.[6] Turner and Seden have reported the cycloaddition of dichloroketene and indene to yield a precursor to 4,5-benzotropolone.[7] Also, Ghasez and co-workers have recently published on a couple of cycloadditions of dichloroketene. It was indicated that this new ketene might be novel as compared to dialkylketenes in that cycloaddition with the unactivated olefin, cyclopentene, occurred readily and in good yield.[8] It is well established that the ease of cycloaddition of dialkylketenes parallels the nucleophilicity of the olefin.

In this paper we report some recent studies concerning the cycloadditions of various olefins with dichloroketene.

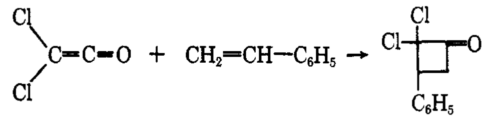
Owing to its extreme reactivity, this new ketene was prepared by both of the methods mentioned above and allowed to undergo cycloaddition *in situ.*

Dichloroketene, prepared by the dehalogenation of trichloroacetyl bromide, reacted with cyclohexene *in situ* at room temperature to yield 8,8-dichlorobicyclo[4.2.0]octan-7-one (1) in 52% yield. The structure of 1 was proved by a combination of elemental analysis and infrared and proton magnetic resonance (pmr) spectra. An infrared band at 1800 cm^{-1} showed that the adduct was a cyclobutanone. The pmr spectrum revealed the presence of the methylene protons at τ 8.2 and the two methinyl protons at τ 5.9 and τ 7.1 in the ratio of 8:1:1. This cycloadduct was also prepared by generating dichloroketene by the dehydrobromination of dichloroacetyl bromide in the presence of cyclohexene.



1

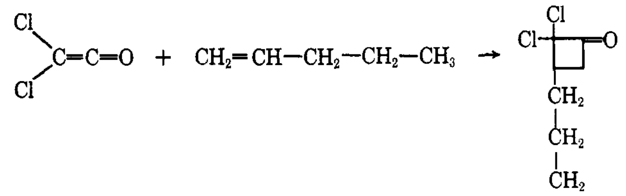
Styrene underwent a 1,2-cycloaddition with dichloroketene to produce 2,2-dichloro-3-phenylcyclobutanone (2) in 19% yield. This cycloadduct could be prepared only by preparing the ketene by the dehydrohalogenation method because styrene was polymerized by the other process.



2

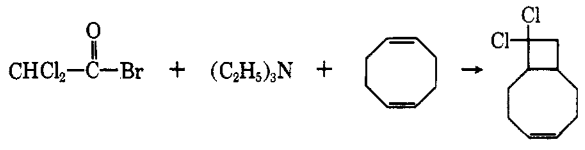
The pmr spectrum showed a methylene group adjacent to a carbonyl group. The methylene groups adjacent to the carbonyl group in cyclobutanone occur at τ 6.97 while the remaining methylene group occurs at τ 8.04.[9] The methylene group in this styrene cycloadduct appeared at τ 6.55. No protons appeared in the τ 8 region where the β protons of cyclobutanone absorb.

The cycloaddition of dichloroketene and 1-pentene occurred readily by preparing the ketene by the dehalogenation method in the presence of the olefin. The cycloadduct 2,2-dichloro-3-(1-propyl)cyclobutanone (3) was obtained in 31% yield. Identification of 3 was based on a combination of elemental analysis and infrared and pmr spectra. This compound could also be readily obtained by synthesizing the ketene by the dehydrohalogenation method in the presence of the olefin.



3

1,5-Cyclooctadiene underwent a 1,2-cycloaddition with dichloroketene to produce 10,10-dichlorobicyclo-[6.2.0]dec-4-en-9-one (4) in 53% yield. The ketene was prepared by the dehydrobromination of dichloroacetyl bromide as illustrated below. The structure of 4 was assigned on the basis of elemental analysis and infrared and pmr spectra.



4

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[1] This work was supported by a National Science Foundation Grant GP-4628 and a Faculty Research Grant, North Texas State University, Denton, Texas.

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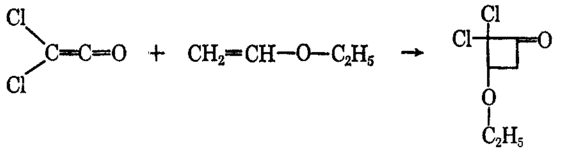
When ethyl vinyl ether was present during the dehydrobromination of dichloroacetyl bromide, the cycloadduct 2,2-dichloro-3-ethoxycyclobutanone (5) was produced in 45% yield.

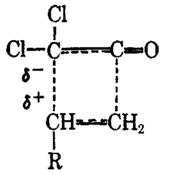


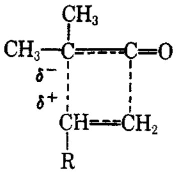
5

Numerous efforts to effect the cycloaddition of dichloroketene with the strongly electrophilic olefin, acrylonitrile, were unsuccessful. Consequently, dichloroketene, like diphenyl and dialkylketenes apparently will not enter into cycloadditions with a strongly electrophilic olefin. Turner and Seden[7] indicated the cycloadduct of dichloroketene and indene was produced in 12% yield. The cycloaddition of dichloroketene and styrene proceeded with difficulty and a yield of only 19% was obtained as indicated above. Since these olefins are somewhat electrophilic, this undoubtedly accounts for the lower yields as they are less reactive than unactivated or activated olefins.

The results of this study would seem to indicate that dichloroketene readily undergoes 1,2-cycloadditions with a variety of olefins. This ketene appears to enter into cycloadditions with nonactivated cyclic and acylic olefins as readily as it does with activated olefins. It seems pertinent to mention that regardless of the two methods of preparing dichloroketene there is a competing polymerization reaction of the ketene which results in a lowering of the yield of cycloadduct. While either of the two methods discussed can be used for dichloroketene cycloadditions, both have their limitations. The dehalogenation method is applicable only for olefins that are not susceptible to polymerization; *e.g.*, ethyl vinyl ether will not undergo cycloaddition with the ketene *in situ* because it polymerizes readily in the presence of the zinc halide. Furan, styrene, conjugated dienes, etc., are also examples of olefins that may not be employed in this particular procedure because of the undesirable polymerization of the olefin. In the dehydrohalogenation method, the amine salt, which is produced as a by-product, is known to catalyze the polymerization of particularly low molecular weight ketenes.[10,11]

Krapcho and Lesser have recently reported on a similar cycloaddition study with dimethylketene and indicated that dimethylketene forms 1,2-cycloaddition products with olefinic substrates in good yields when the ketene is passed into the olefin at elevated temperatures.[12] Because of the competing polymerization reaction of dichloroketene and the ease of the cycloadditions at room temperature and below, it would appear that dichloroketene is somewhat more reactive than dimethylketene toward unactivated olefins. Also, considerably more vigorous conditions are required for dimethylketene cycloadditions. There is recent evidence in the literature which suggests that these cycloaddition reactions proceed by a near concerted process with some charge separation in the transition state.[13,14] If this is the case in these cycloaddition reactions, the following two proposed transition states might explain why dichloroketene is more reactive with unactivated olefins than dimethylketene.





The chlorine atoms would be more effective in stabilizing the carbanionic character of the α-carbon atom and thus lower the energy requirements for the reaction. Also, these transition states suggest that cycloaddition with a strongly electrophilic olefin (R is electron withdrawing) would be difficult because the electron-withdrawing substituent is attached to a carbon atom which possesses carbonium ion character.

In conclusion, this study suggests that dichloroketene is a valuable intermediate for the synthesis of a vast array of substituted cyclobutanones, and while this ketene appears to be somewhat more reactive than dimethylketene with unactivated olefins, it is very similar in most respects.

Experimental Section

Dichloroacetyl bromide and trichloroacetyl bromide were prepared from the corresponding acids and phosphorous tribromide.[15] All of the solvents employed in this study were dried by refluxing and distilling from lithium aluminum hydride through a 30-plate Oldershaw column. All of the olefins used were commercially available. The activation of zinc for the dehalogenation reaction has already been described.[3] The pmr spectra were recorded on a Varian A-60 instrument at 60 Mc.

8,8-Dichlorobicyclo[4.2.0]octan-7-one (1).—To a stirred mixture containing 200 ml of dry ether, 41.0 g (0.63 mole) of zinc dust activated with copper and 64 ml (0.63 mole) of cyclohexene was added dropwise a solution of 28.0 g (0.12 mole) of freshly distilled trichloroacetyl bromide in 50 ml of dry ether. At the conclusion of the exothermic reaction, the ether solution was separated from the unreacted zinc and extracted with 200 ml of hexane which resulted in the precipitation of the zinc halide. The solution was decanted from the residue and the solvents were evaporated. The residue was distilled at reduced pressure to yield 10.5 g (52%) of 8,8-dichlorobicyclo[4.2.0]octan-7-one at 93–94° (2.5 mm). Infrared analysis showed a cyclobutanone carbonyl absorption at 1800 cm^{-1}. The pmr ($CDCl_3$) data was discussed above.

Anal. Calcd for $C_8H_{10}Cl_2O$: C, 50.08; H, 5.18; Cl, 36.80; mol wt, 193. Found: C, 50.32; H, 5.47; Cl, 36.43; mol wt, 190.

2,2-Dichloro-3-phenylcyclobutanone (2).—A solution of 77 g (0.4 mole) of dichloroacetyl bromide in 50 ml of dry hexane was added to a stirred refluxing solution of 200 ml of dry hexane, 61 ml (45 g, 0.45 mole) of triethylamine, and 140 ml (125 g, 1.2 mole) of styrene. The reaction mixture was refluxed for 6 hr and allowed to stand overnight at room temperature. The mixture was filtered and the filtrate was washed with water until the washings were neutral. The solvent was then evaporated by a stream of nitrogen and the residue was distilled under reduced pressure. There was obtained 13 g (19%) of 2,2-dichloro-2-phenylcyclobutanone at 103° (1.6 mm): infrared absorption (smear), 1806 cm^{-1}; pmr ($CHCl_3$), a multiplet centered at τ 2.8 (phenyl protons), a multiplet centered at τ 6.0 (methinyl proton), and a multiplet centered at τ 6.55 (methylene protons). The peak areas were in the ratio of 8:1:2.

Anal. Calcd for $C_{10}H_8Cl_2O$: C, 55.81; H, 3.72. Found: C, 55.62; H, 3.53.

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2,2-Dichloro-3-(1-propyl)cyclobutanone (3).—A 50.0-g (0.22 mole) portion of freshly distilled trichloroacetyl bromide in 50 ml of dry ether was added dropwise to a stirred mixture of 250 ml of dry ether, 120 ml (1.11 moles) of 1-pentene and 57.5 g (0.88 mole) of zinc dust activated with copper. The mixture was cautiously warmed to initiate the exothermic reaction. The reaction solution was separated from the unreacted zinc and extracted with hexane. The solvents were evaporated to yield 8.0 g (31%) of 2,2-dichloro-3-(1-propyl)cyclobutanone at 69.5–70° (1.5 mm): infrared absorption smear, 1800 cm^{-1}. A pmr spectrum in $CDCl_3$ revealed a complex multiplet centered at τ 8.8 characteristic of the *n*-propyl group and another complex multiplet centered at τ 7.0 which had an area that was three-sevenths of the multiplet centered at τ 8.8.

Anal. Calcd for $C_7H_{10}Cl_2O$: C, 46.41; H, 5.52; mol wt, 181. Found: C, 46.66; H, 5.65; mol wt, 188.

10,10-Dichlorobicyclo[6.2.0]dec-4-en-9-one (4).—To a stirred refluxing solution containing 200 ml of dry hexane, 45.7 ml (0.33 mole) of triethylamine and 127 ml (1.04 moles) of 1,5-cyclooctadiene was added dropwise a solution of 50 g (0.26 mole) of freshly distilled dichloroacetyl bromide in 50 ml of dry hexane. The reaction mixture was refluxed 4 hr and the amine salt was removed by filtration. The filtrate was washed with water and dried over anhydrous magnesium sulfate. The solvent and excess olefin were removed by distillation and the residue was distilled to yield 24 g (53%) of 10,10-dichlorobicyclo[6.2.0]dec-4-en-9-one at 112° (1.0 mm): infrared absorption (smear), 1806 (s) and 1650 cm^{-1}; pmr spectrum ($CHCl_3$), complex multiplet centered at τ 7.9 (methylene protons), multiplet at τ 6.6 and 5.0 (methinyl protons), and multiplet centered at τ 3.3 (vinyl protons). The peak areas were in the ratio of 8:1:1:2.

Anal. Calcd for $C_{10}H_{12}Cl_2O$: C, 54.79; H, 5.48; mol wt, 219. Found: C, 55.04; H, 5.75; mol wt, 227.

2,2-Dichloro-3-ethoxycyclobutanone (5).—A solution of 54 g (0.28 mole) of freshly distilled dichloroacetyl bromide in 50 ml of dry ether was added dropwise to a stirred solution of 200 ml of dry ether, 70 ml (0.74 mole) of ethyl vinyl ether, and 41 ml (0.3 mole) of triethylamine at 0–5°. The reaction mixture was stirred 3 hr. The triethylammonium bromide was removed by filtration and the filtrate was washed with water and dried over anhydrous magnesium sulfate. The solvent was evaporated and the residue was distilled to yield 18.5 g (45%) of 2,2-dichloro-3-ethoxycyclobutanone at 91–94° (2.5 mm): infrared absorption (smear), 1806 cm^{-1}.

Anal. Calcd for $C_6H_8Cl_2O_2$: C, 39.34; H, 4.37. Found: C, 39.41; H, 4.64.

Registry No.—**1**, 13866-27-8; **2**, 13866-28-9; **3**, 13866-29-0; **4**, 13866-30-3; **5**, 13866-31-4; dichloroketene, 4591-28-0.

Free Radicals from the Irradiation of *o*-Nitrobenzyl Compounds

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Pioneering Research Division, U. S. Army Natick Laboratories, Natick, Massachusetts 01760

Received May 22, 1967

Photochromism in nitrobenzyl compounds requires only the presence of a nitro and >C–H group *ortho* to each other.[2] The color change is believed to be due to formation (eq 1) of the *aci*-nitro structure.[2,3] We present here evidence which indicates that simple *o*-nitroalkylbenzenes undergo still another process when irradiated with ultraviolet light.

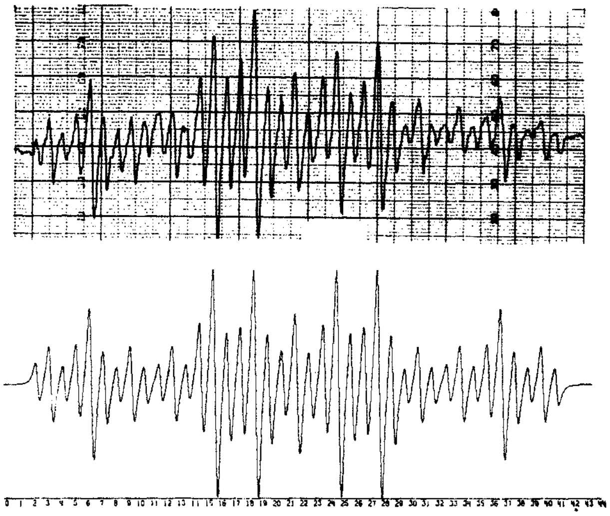


Figure 1.—Experimental spectrum obtained from irradiation of *o*-nitrocumene and simulated spectrum using splitting constants in text and a line width of 0.32 gauss.

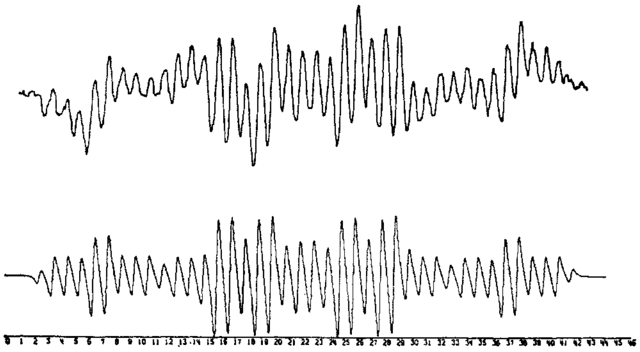
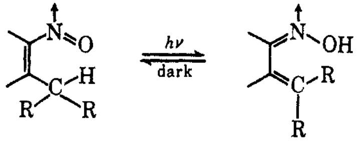


Figure 2.—Experimental spectrum obtained from irradiation of *o*-nitroethylbenzene and simulated spectrum using splitting constants in text and a line width of 0.32 gauss.



(1)

Irradiation of deoxygenated *o*-nitrocumene (neat) gave within 30 sec copious amounts of a single radical species. A 39-peak esr spectrum was recorded with the analysis as follows: $A^N(1\ N) = 9.1 \pm 0.1$ gauss, $A^H(1\ H) = 12.1 \pm 0.1$ gauss, $A^H(2\ H) = 3.0 \pm 0.1$ gauss, $A^H(2\ H) = 1.0 \pm 0.1$ gauss. The irradiation of neat *o*-nitroethylbenzene gave moderate amounts of a radical with a 40-peak esr spectrum. The splittings determined were $A^N(1\ N) = 9.1 \pm 0.1$ gauss, $A^H(1\ H) = 12.1 \pm 0.1$ gauss, $A^H(2\ H) = 3.0 \pm 0.1$ gauss, and $A^H(3\ H) = 1.0 \pm 0.1$ gauss. The experimental spectra together with theoretical spectra calculated from the above splitting constants are shown in Figures 1 and 2.[4] Continual irradiation of neat *o*-nitrotoluene gave only very small amounts of a radical with some hyperfine structure. An analysis could not be made because of the low radical concentration.

These radicals were stable for days and could also

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[1] To whom inquiries should be addressed at the Mobil Oil Corp. Field Research Laboratory, Dallas, Texas 75221.

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[4] Alternating line widths and a less well-resolved experimental spectrum in Figure 2 cause minor deviations in spectrum amplitudes.