Anal. Calcd for $C_{22}H_{40}O_3$: C, 75.01; H, 11.3. Found: C, 74.72; H, 11.1.

1-O-Hexadec-1′,2′-dienylglycerol (5).—Crude product **4** (4 g, 11.3 mmoles) was hydrolyzed with[17] 6.2 g (40 mmoles) of finely powdered boric acid in 20 ml of methyl cellosolve in a boiling water bath for 1 hr. The residue was dissolved in Skellysolve F and cooled at −10°F overnight to yield a yellow precipitate. This was collected by filtration in the cold to obtain 0.357 g of **5** in 10% yield: $n^{24.5}\text{D}$ 1.4727; $\nu_{\max}^{\text{smear}}$ 1965 (OC=C=C–), 3420 cm^{-1} (OH).

Anal. Calcd for $C_{19}H_{36}O_3$: C, 73.08; H, 11.54. Found: C, 72.93; H, 11.26.

1-O-Hexadec-1′,2′-dienyl-2,3-di-O-palmitoylglycerol (**6**) was prepared by acylation of **5** (0.4 g, 1.25 mmoles) with palmitoyl chloride (1.05 g, 3.8 mmoles) in the presnce of 8 ml of pyridine and in 20 ml of dry $CHCl_3$. The product (**6**) was obtained by recrystallization from acetone at 0°: yield, 89%; mp 38–39°; $\nu_{\max}^{\text{smear}}$ 1755 (ester C=O), 1950 cm^{-1} (OC=C=C).

Anal. Calcd for $C_{51}H_{96}O_5$: C, 77.67; H, 12.18. Found: C, 77.67, H, 12.32.

1-O-Hexadec-1′,2′-dienyl-2,3-di-O-oleylglycerol was prepared as outlined above and obtained as an oil in 60% yield: $\nu_{\max}^{\text{smear}}$ 1760 (ester C=O), 1970 cm^{-1} (–OC=C=C).

Anal. Calcd for $C_{55}H_{100}O_5$: C, 78.56; H, 11.91. Found: C, 78.63; H, 11.90.

Reaction of Iodine with 1-O-Hept-1′,2′-dienyl-2,3-O-isopropylideneglycerol.—To a solution of 1-O-hept-1′,2′-dienyl-2,3-O-isopropylideneglycerol in methanol was added 0.1 *N* iodine solution until there was a permanent yellow color. The immiscible yellow liquid which separated was recovered by ether extraction: $\nu_{\max}^{\text{smear}}$ 1710 (aldehyde C=O), 1610 (conjugated C=C), 27.50 cm^{-1} (CH stretching of aldehyde); orange-red 2,4-dinitrophenylhydrazone derivative had mp 172–173° dec; $\lambda_{\max}^{\text{EtOH}}$ 372 mμ ($\epsilon_{\max}$ 28,000).

Anal. Calcd for $C_{13}H_{15}N_4O_4I$: C, 37.32; H, 3.59; N, 13.40; I, 30.3. Found: C, 37.30; H, 3.69; N, 13.26; I, 29.10.

Registry No.—**2,** 13866-75-6; **3,** 13866-76-7; **5,** 13866-77-8; **6,** 13866-78-9; 1-O-hexadec-1′,2′-dienyl-2,3-di-O-oleylglycerol, 13970-35-9.

[17] L. Hartman, *J. Chem. Soc.*, 4134 (1959).

Enolization of Ketones. III.[1] The Rate and Orientation of Acid-Catalyzed Deuteration of Some Methyl Ketones

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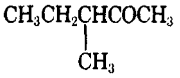
The acid-catalyzed enolization of ketones has been studied by means of halogenation, racemization of optically active ketones, and deuteration experiments.[2–9] Of these methods, halogenation has been most commonly used.

In 1935, Bartlett and Stauffer studied the acid-catalyzed enolization of some secondary butyl ketones.[6] From a comparison between the rate of racemization of the optically active ketones and their over-all rate of iodination, the rate of reaction at each of the α carbons and the orientation of substitution were calculated. Bartlett and Stauffer found no general rules for the orientation of substitution.[6]

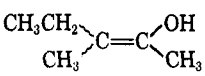
In 1951, Cardwell and Kilner studied the orientation of the enolization of a number of ketones by halogenation experiments.[8] From a comparison with the rate of iodination for the same ketones determined by Dawson,[10] the relative rate of halogenation of each of the two α carbons could be calculated. The orientation was found to follow the Saytzeff rule and this investigation has been considered as a classic investigation of the orientation of enolization as well as of hyperconjugation.[8,11]

3-Methyl-2-pentanone (I) was studied in both investigations. Bartlett and Stauffer reported a value

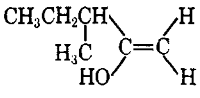


$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCOCH_3$

I



II



III

for the orientation of enolization, "3-enol"/"1-enol" = II/III = 0.22, while Cardwell and Kilner found the same ratio (II/III) to be 3.8.[6,8] Cardwell and Kilner explained the large difference to be due to the use of very incompletely resolved ketone in the racemization experiment.[8] However, in our opinion it is difficult to see how this could influence the rate of racemization and therefore the reason for the discrepancy must be found elsewhere.

In the halogenation experiments, the separation of the two α-monohalo isomers and the polyhalo ketones was made by distillation and, as already pointed out by Cardwell and Kilner, it is difficult to estimate the accuracy of these analyses. Another objection that can be raised against these results is that rearrangements can occur during the syntheses and the long distillations of the halogenated ketones.[12]

Nmr spectroscopy has proven to be an excellent tool with which to follow the deuteration of ketones. Here the orientation and the rate of reaction can be estimated in the same experiment.[13,14] In a recent paper, one of us studied the orientation of deuteration in 2-butanone in both acid- and base-catalyzed reactions. In the case of acid-catalyzed reactions, the orientation of deuteration was found to be approximately the same as the orientation of halogenation.[13,15]

Later, Bothner-By and Sun, who used the same nmr technique, confirmed the orientation for the acid- and base-catalyzed deuteration of 2-butanone.[16] In addition to 2-butanone, these authors also studied the deuteration of acetone, 3-pentanone, and methoxyacetone. Since 3-pentanone was found to enolize more slowly

[1] Part I and II of this series: *Acta Chem. Scand.*, **20**, 2236, 2305 (1966).

[2] A. Lapworth, *J. Chem. Soc.*, **85**, 30 (1904).

[3] E. D. Hughes, H. B. Watson, and E. D. Yates, *ibid.*, 3318 (1931).

[4] H. B. Watson and E. D. Yates, *ibid.*, 1207 (1932).

[5] C. K. Ingold and C. L. Wilson, *ibid.*, 773 (1934).

[6] P. D. Bartlett and C. H. Stauffer, *J. Am. Chem. Soc.*, **57**, 2580 (1935).

[7] J. R. Catch, D. F. Elliott, D. H. Hey, and E. R. H. Jones, *J. Chem. Soc.*, 272 (1948); J. R. Catch, D. H. Hey, E. R. H. Jones, and W. Wilson, *ibid.*, 276 (1948).

[8] H. M. E. Cardwell and A. H. E. Kilner, *ibid.*, 2430 (1951).

[9] C. Rappe, *Arkiv Kemi*, **24**, 321 (1965).

[10] H. M. Dawson and R. Wheatley, *J. Chem. Soc.*, **97**, 2048 (1910); H. M. Dawson and H. Ark, *ibid.*, **99**, 1740 (1911).

[11] (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp 557–560; (b) E. Müller, "Neuere Anschauungen der Organischen Chemie," Springer-Verlag, Berlin, 1957, pp 420–422; (c) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, pp 382–384.

[12] C. Rappe, *Arkiv Kemi*, **23**, 81 (1964); C. Rappe, *ibid.*, **24**, 73 (1965).

[13] C. Rappe, *Acta Chem. Scand.*, **20**, 2236 (1966).

[14] J. Hine, J. G. Houston, J. H. Jensen, and J. Mulders, *J. Am. Chem. Soc.*, **87**, 5050 (1965); J. Warkentin and O. S. Tee, *ibid.*, **88**, 5540 (1966).

[15] In the case of 2-butanone, K_D has been determined as 2.7[14] and K_{hal} as 2.4–2.5: C. Rappe, *Acta Chem. Scand.*, in press.

[16] A. A. Bothner-By and C. Sun, *J. Org. Chem.*, **32**, 492 (1967).

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS

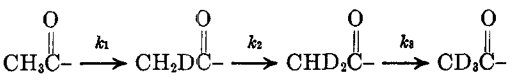
Ketone	$k_1 \times 10^5$, sec^{-1} CH	CH	CH	K_D	k_{Br-CH_3}[a]	k_{Br_2-CH}[a]	k_{Br-CH}[a]	K_{Br}[a]
Acetone	1.83[b] 0.92	...	...	...	50	..	..	...
2-Butanone	1.39	2.68	...	1.9	28	76	..	2.7
2-Pentanone	1.32	2.08	...	1.6	35	59	..	1.7
2-Hexanone	1.25	2.18	...	1.7	25	85	..	3.3
2-Heptanone	1.42	2.06	...	1.5	37	58	..	1.5
3-Methyl-2-butanone	1.47	...	1.18	0.80	17	..	52	3.0
3-Methyl-2-pentanone	1.55	...	0.29	0.19	10	..	38	3.8
3-Ethyl-2-pentanone	1.32	...	0.16	0.12	..	..	..	...
Pinacolone	1.62	...	...	...	46	..	..	...
4-Methyl-2-pentanone	(1.6)[c]	(1.2)[c]	...	(0.75)[c]	41	45	..	1.1
4,4-Dimethyl-2-pentanone	1.93	0.56	...	0.29	..	..	..	...

[a] Relative values reported by Cardwell and Kilner.[8] [b] This value was obtained by multiplying $k_{obsd\ CH_3}$ by a factor of 6 and dividing by a factor of 2. [c] These values are obtained by an indirect method. K_{Br} was determined as 0.75. It was assumed that $K_D = K_{Br} = 0.75$. The total rate of deuteration was roughly estimated from the increasing DOH peak.

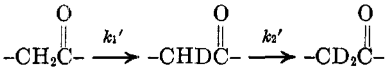
than acetone, they suggest that the polar effect of alkyl substituents retards acid-catalyzed enolization. This seems to be an oversimplification since in 2-butanone the methylene deuteration is faster than the methyl deuteration. Moreover, since the study was limited to only three ketones, it is difficult to differentiate between the inductive, steric, and hyperconjugative effect of an alkyl group.

In the present investigation, we have studied the deuteration of a number of methyl ketones other than 2-butanone. Making first-order plots of the data obtained in the deuteration experiments, straight lines were obtained up to about 40% deuteration. For methyl, methylene, and methine groups, the following k values were obtained: $k_{obsd\ CH_3}$, $k_{obsd\ CH_2}$, and $k_{obsd\ CH}$, respectively.

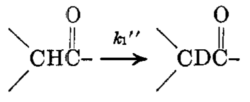
The stepwise deuteration of methyl, methylene, and methine groups of ketones were



$$CH_3\overset{O}{\overset{\|}{C}}- \xrightarrow{k_1} CH_2D\overset{O}{\overset{\|}{C}}- \xrightarrow{k_2} CHD_2\overset{O}{\overset{\|}{C}}- \xrightarrow{k_3} CD_3\overset{O}{\overset{\|}{C}}- \quad (1)$$



$$-CH_2\overset{O}{\overset{\|}{C}}- \xrightarrow{k_1'} -CHD\overset{O}{\overset{\|}{C}}- \xrightarrow{k_2'} -CD_2\overset{O}{\overset{\|}{C}}- \quad (2)$$



$$>CH\overset{O}{\overset{\|}{C}}- \xrightarrow{k_1''} >CD\overset{O}{\overset{\|}{C}}- \quad (3)$$

If we neglect a presumably small secondary isotope effect, the rate of proton removal will depend upon the number of protons in the groups. Thus

$$k_1 = 3k_3 \quad (4)$$

$$k_2 = 2k_3 \quad (5)$$

$$k_1' = 2k_2' \quad (6)$$

Previously it was shown[13] that

$$k_1 = 3k_{obsd\ CH_3} \quad (7)$$

$$k_1' = 2k_{obsd\ CH_2} \quad (8)$$

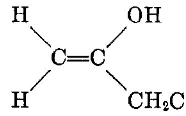
$$k_1'' = k_{obsd\ CH} \quad (9)$$

Our results are summarized in Table I. For comparison, the relative rate constants determined by Cardwell and Kilner[8] are also given in the table. In addition to the rate constants, it was of interest to calculate and compare the orientation of the deuteration with the orientation of bromination as given by Cardwell and Kilner.[8] This can be done by a calculation of the K_D and K_{Br} values, where K_D and K_{Br} are defined as k_{CH_2}/k_{CH_3} or k_{CH}/k_{CH_3} for the two reactions.

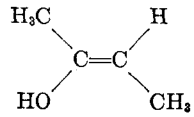
As mentioned above, acid-catalyzed enolization of ketones is considered to follow the Saytzeff rule and to be an example of a reaction controlled by hyperconjugative factors. According to this hypothesis, an increasing number of hydrogens stabilizing the enol by hyperconjugation would increase the enolization rate.[8,11] On the other hand, the base-catalyzed process is considered to be controlled by inductive effects.[11,17,18]

The four ketones acetone, 2-butanone, 3-methyl-2-butanone, and pinacolone have 3, 2, 1, and 0 hydrogens, respectively, stabilizing the "1-enol," and the rate for the methyl deuteration could be expected to decrease in the series. Acetone was found to have the highest value, but for the other three ketones the opposite trend is in fact observed. Examining the rate constants for all the ketones in Table I, it seems to be a general feature that a large and bulky group increases the rate of methyl deuteration.

The methylene group of an unbranched methyl ketone is in all cases deuterated faster than the methyl group, which is in accordance with the theory of hyperconjugation. By an extended Hückel calculation,[13] it was recently found that in the case of 2-butanone the *trans*-enol V is favored by about 1.4 kcal/mole over the enol IV.



IV



V

The methylene group of 2-butanone is deuterated about 20–30% faster than the methylene groups of the higher homologs, which all are of about the same magnitude. The reason for the pronouncedly slower rate of the methylene deuteration in 4-methyl- and 4,4-dimethyl-2-pentanone seems to be found in the increased steric interaction arising from the isopropyl and *t*-butyl groups, *i.e.*, a *cis* effect.

The deuteration of the methine group of 3-methyl-2-butanone is less than half as fast as the deuteration of the methylene group of 2-butanone. The in-

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(17) H. M. E. Cardwell, *J. Chem. Soc.*, 2442 (1951).

(18) H. Shechter, M. J. Collis, R. Dessy, Y. Okuzumi, and A. Chen, *J. Am. Chem. Soc.*, **84**, 2905 (1962).

troduction of a second methyl group on the α carbon, while enhancing the possibilities for hyperconjugation, also introduces an inductive effect and a pronounced *cis* effect in the presumably planar transition state[18] and one or both of these effects seem to be responsible for the decrease in the deuteration rate. This effect has previously been observed in the enol content of some β diketones.[19]

The higher homologs, which contain methine groups, have a still much slower rate for the deuteration than 3-methyl-2-pentanone. Within this series, the inductive effect, the *cis* effect, and hyperconjugation operate in the same direction, but the large differences observed indicate that the *cis* effect probably dominates.

Since the K_D values are defined as the quotient of the rate constants discussed above, they will be treated rather briefly here. The K_D values for the unbranched methyl ketones are all in the same region, 1.5–2.0, indicating that the rate of enolization of the methylene group is slightly favored over that of the methyl group. On the contrary, the K_D values of branched methyl ketones are lower than 1.0. This means that in all branched methyl ketones studied, the substitution of the methyl group dominates. In the more branched ketones, this effect is very obvious.

As previously mentioned, the values for the reported[6,8] orientation of the substitution of 3-methyl-2-pentanone are contradictory. Our result is K_D = II/III = 0.19, which is in good accordance with the value reported by Bartlett and Stauffer.[6]

In order to determine the orientation of the halogenation (K_{hal} values), preliminary experiments were performed where the crude products from the halogenation of 2-pentanone, 3-methyl-2-butanone, and 3-methyl-2-pentanone were analyzed by nmr. In this investigation, we used chlorine and bromine, an aqueous medium, and a dioxane–water mixture. The results are collected in Table II.

TABLE II

ORIENTATION OF HALOGENATIONS[a]

Ketone	K_D	K_{Cl} A[b]	K_{Cl} B[c]	K_{Br} A	K_{Br} B
2-Pentanone	1.6	1.5	...	1.5	...
3-Methyl-2-butanone	0.8	1.0	1.0	1.1	1.1
3-Methyl-2-pentanone	0.2	0.5	0.5	0.5	0.5

[a] See also ref 15. [b] A, aqueous medium. [c] B, dioxane–water.

Most of our knowledge of the orientation of the acid-catalyzed enolization of ketones is based on halogenation experiments.[2–9] In the present investigation, we have observed a pronounced discrepancy between the orientation of deuteration and the accepted rules for the acid-catalyzed enolization of ketones.[8,11] This discrepancy can be discussed in two ways.

1. The two investigations were performed under different conditions. In the bromination experiments, Cardwell and Kilner used an aqueous solution with an excess of acid, while in our deuterations we have used an organic solvent (dioxane–D_2O) and only catalytic amounts of acid. For example, it can be mentioned that in aqueous media 2-butanone was found to have K_D = 2.4–2.5 for the acid-catalyzed deuteration; however, in the present investigation we obtained K_D = 1.9.[13] The same effect has been recently reported for the base-catalyzed deuteration of 2-butanone.[14]

2. Owing to cursory analytical methods and rearrangements during the synthesis and work-up, the K_{Br} values reported previously can be incorrect. As chloro ketones in general do not rearrange,[12] it is more safe to study the orientation of chlorination instead of bromination.

The difference in orientation between the halogenations (Table II) and deuterations are in general small.[15] Since the solvent and the nature of halogen were of minor importance for the orientation of the halogenation, these differences may be of significance and will be discussed in a forthcoming paper.

Our investigation shows that the generally accepted rules for the orientation of the acid-catalyzed enolization of ketones in several cases are incorrect.[8,11] At the present state, no general rules can be given for the orientation and therefore they are best determined from case to case. This can be easily done by deuterations using nmr technique.[13,14,16] The deuteration of ketones other than those discussed in the present investigation is under study. This investigation will include cycloalkanones, cycloalkyl methyl ketones, and aromatic ketones.

Experimental Section

Nmr measurements were carried out on a Varian A-60 spectrometer equipped with a C-1024 time averaging computer. Chromatograms were obtained from a Perkin-Elmer F-21 gas chromatograph.

Materials.—All the ketones studied, except 4,4-dimethyl-2-pentanone,[20] were obtained commercially. Nmr spectra were recorded neat on the ketones and no extraneous peaks were observed. In addition, the ketones were checked chromatographically and found to be >99% in purity. Dioxane and deuterium oxide (99.7%) were used as supplied. The acid catalyst was prepared by diluting 0.685 g of 20% deuterium chloride in deuterium oxide to 25 ml with additional deuterium oxide.

Kinetic Runs.—Kinetic runs were carried out in one-phase systems in duplicate directly in capped nmr tubes. The tubes were kept at constant temperature (40.2 ± 0.2°) between analyses in a thermostated oil bath. The probe temperature maintained itself at about 39° over the course of the investigation.

A typical run consisted of 0.5 ml of catalyst, 0.8 ml of dioxane, and 0.2 ml of ketone. Exceptions were 3-ethyl-2-pentanone (0.1 ml), 4,4-dimethyl-2-pentanone (0.1 ml), pinacolone (0.15 ml), and 2-heptanone (0.1 ml).[21] Integrals were recorded until a predominant trace was apparent, thus averaging to zero temporary instabilities within the instrument. Each analysis was internally referenced by integrating over the protons of an unreacting group within the ketone[13,14,16] or by integrating over the DOH peak, which gives a constant when summed with the remaining area of the deuterating groups. The first-order rate constants are estimated to be accurate within ±10% for those ketones in which 0.2 ml of ketone was employed and somewhat less (±15%) for the remaining runs. Deuteration was determined to be first order in ketone for 2-butanone in the concentration range employed with the aid of the time-average computer. The deuterations are thereby assumed to be first order for the other ketones investigated.

Registry No.—Acetone, 67-64-1; 2-butanone, 78-93-3; 2-pentanone, 107-87-9; 2-hexanone, 591-78-6; 2-heptanone, 110-43-0; 3-methyl-2-butanone, 563-80-4; 3-methyl-2-pentanone, 565-61-7; 3-ethyl-2-pentanone,

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[19] See ref 11c, p 376.

[20] W. A. Mosher and J. C. Cox, Jr., *J. Am. Chem. Soc.*, **72**, 3701 (1950).

[21] The first-order rate constants have been corrected for the apparent change in acid concentration owing to change in total volume.

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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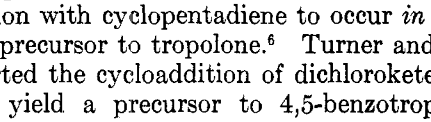
Received April 28, 1967

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.

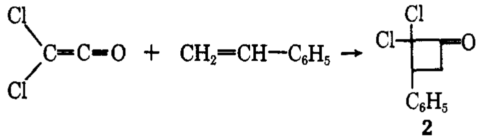
Owing to its extreme reactivity, this new ketene was prepared by both of the methods mentioned above and allowed to undergo cycloaddition *in situ*.

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

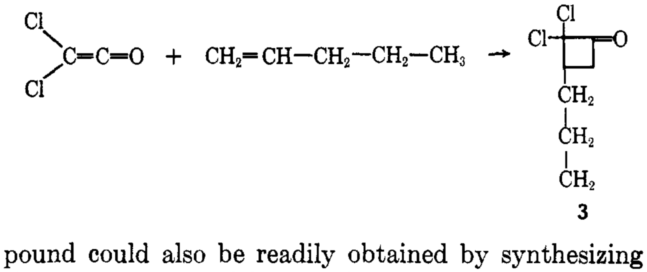
Styrene underwent a 1,2-cycloaddition with dichloroketene to produce 2,2-dichloro-3-phenylcyclobutanone (2) in 19% yield. This cycloadduct could be prepared only by preparing the ketene by the dehydrohalogenation method because styrene was polymerized by the other process.



2

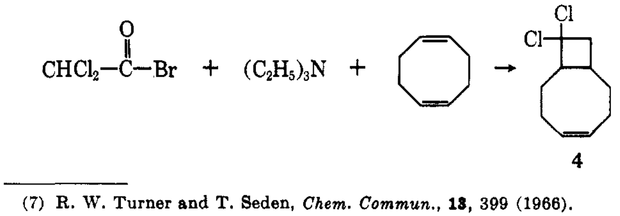
The pmr spectrum showed a methylene group adjacent to a carbonyl group. The methylene groups adjacent to the carbonyl group in cyclobutanone occur at τ 6.97 while the remaining methylene group occurs at τ 8.04.[9] The methylene group in this styrene cycloadduct appeared at τ 6.55. No protons appeared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