Tetrahedron Letters No.35, pp. 3377-3381, 1967. Pergamon Press Ltd. Printed in Great Britain.

REACTION OF TROPONE WITH DICHLOROKETENE

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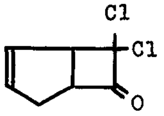
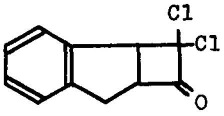
(Received in USA 2 June 1967)

The generation and chemistry of halogenated ketenes has experienced popularity in recent literature (1,2,3). Dichloroketene reportedly forms the cycloadducts I and II with cyclopentadiene (4) and indene (5) respectively.

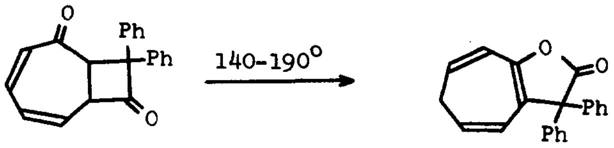


I



II

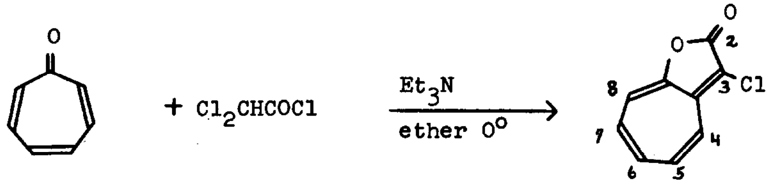
Jutz (6) has reported the formation and quinoline-catalyzed isomerization of the tropone-diphenylketene adduct III. Kende (7) has recently established the structure of the rearrangement product as the lactone IV as well as the fact that the isomerization occurs thermally even in the absence of base.



III

IV

We wish to communicate the reaction of tropone with dichloroketene yielding the heptafulvene derivative V. Dropwise addition of a solution of 50 mmoles of purified triethylamine in 20 ml of ether over a 20 min. period to a solution of 20 mmoles of tropone and 40 mmoles of dichloroacetyl chloride in 50 ml of ether at 0° under nitrogen resulted in the immediate precipitation of tri-



V

ethylamine hydrochloride. After stirring for 18 hr overnight at room temperature the reaction mixture was filtered, and the residue after solvent removal chromatographed over Florisil (benzene-ether 8:2). Sublimation of the crude product (80°C, 0.05 mm) followed by recrystallization from chloroform-cyclohexane afforded yellow-orange needles of m.p. 179-180° in approximately 19% yield, Anal. Calcd. for $C_9H_5O_2Cl$: C, 59.85; H, 2.79; Cl, 19.63; mol. wt. 182. Found: C, 59.86; H, 2.86; Cl, 19.65; mol. wt., mass spectrum m/e 182, osmometric mol. wt. in chloroform 186; $\nu_{max}^{CHCl_3}$ (cm^{-1}) 3030 (w), 1780 (m), 1755 (s), 1605 (m), 1550 (m), 1515 (m), 1420 (m), 1300 (m), 1270 (m), 1050 (m); $\lambda_{max}^{C_2H_5OH}$ (mμ) 399 (ε 11,600), 382 (12,400), 257 (17,500), 224 (11,300); $\lambda_{max}^{cyclohexane}$ 400 (8310), 388 (sh) (8840), 377.5 (11,200), 366 (sh) (9790), 257 (16,700), 232 (sh) (8,260); nmr ($CDCl_3$) in ppm from tms, FIG.1.* The complex multiplets at 7.00 ppm (3H) and 7.25 ppm (2H) are assigned to protons 4,6,8 and 5,7 respectively.

The microanalytical and molecular weight data are clearly consistent with a 1:1 adduct of tropone and dichloroketene minus the elements HCl. On the basis of the above data, the heptafulvene structure V was assigned.

Further conclusive evidence lies in a comparison of the ultraviolet spectrum of V with that of the model system VI reported by Seto (8).

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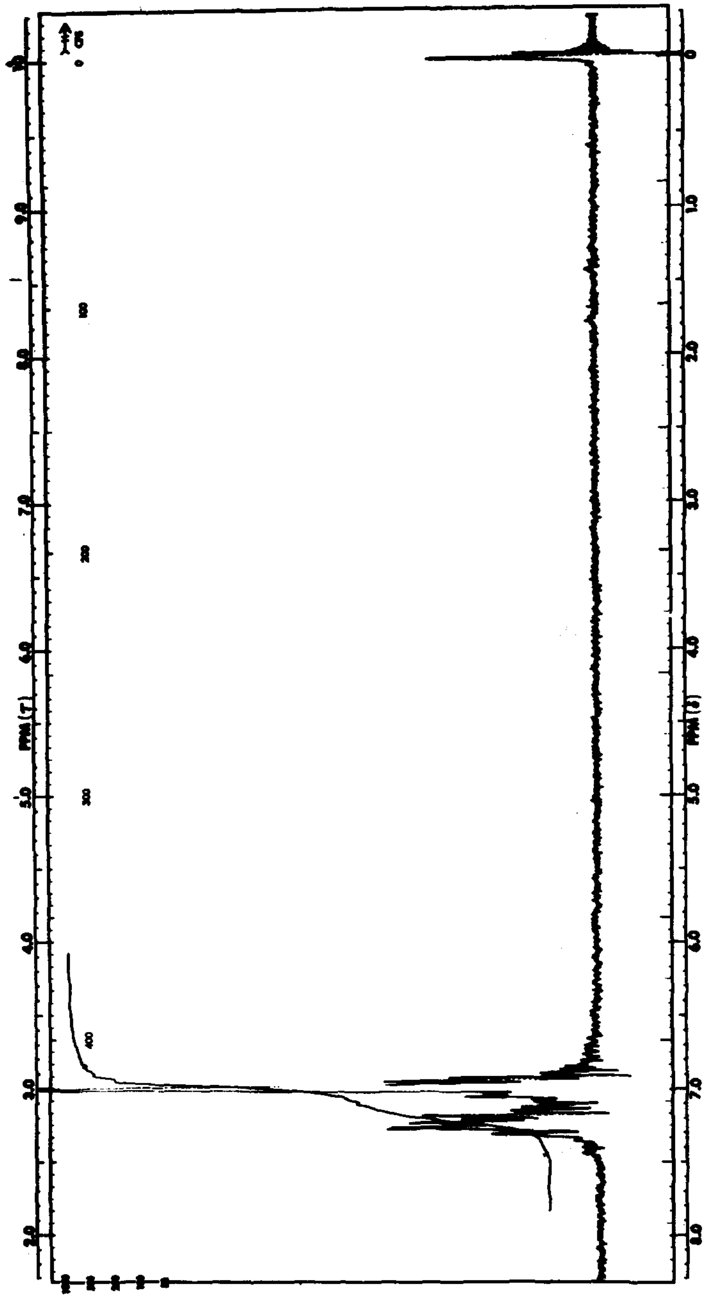
* The Hitachi RMU-6D mass spectrometer as well as the Varian A-60A nmr spectrometer used in this work were purchased through a National Science Foundation major equipment grant to Brown University.

FIG. I


10
9.0
8.0
7.0
6.0
PPM(τ)
5.0
4.0
3.0
2.0
0
100
200
300
400
0
1.0
2.0
3.0
4.0
PPM(δ)
5.0
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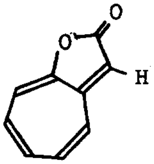
8.0



VI

$\lambda_{max}^{CH_3OH}$	(mμ)	(log ε)
	250	(4.36)
	373	(4.19)
	387	(4.21)

The intermediacy of dichloroketene was established by its generation in the <u>absence of tropone</u>. Dichloroacetyl chloride (20 mmoles) was dissolved in 25 ml of ether and cooled in an ice-salt bath to -7°. Triethylamine (30 mmoles) in 25 ml of ether was added dropwise over a 20 min. period. After 20 additional min. a sample of the reaction mixture was concentrated and subjected to vapor phase chromatography* which indicated the complete absence of dichloroacetyl chloride. After filtration, addition of tropone (5 mmoles), and warming to room temperature followed by work-up as before, compound V was obtained in comparable yield.

Kende's (8) mechanistic study of the thermal isomerization of III revealed that the first step involves cleavage of the $-\underset{H}{\overset{|}{C}}-\overset{|}{C}=O$ cyclobutanone bond followed by reclosure to an intermediate lactone which subsequently undergoes 1,5 hydrogen transfer to give lactone IV. In our hands, we have been unable to detect the presence of cyclobutanone VII spectroscopically at low temperatures. As a result we cannot preclude the alternative possibility of an initial nucleophilic attack of the tropone oxygen on the electrophilic dichloroketene to give an intermediate tropylium ion IX which would suffer ring closure to X and

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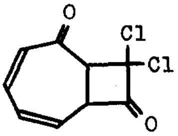
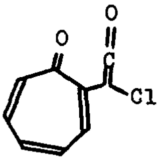
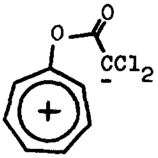
* Analysis was performed with a 5 ft column, 15% carbowax 20 M on chromosorb W, DMCS, A/W, 80/100 mesh at 95°. The retention time of dichloroacetyl chloride under these conditions was 3.88 min.



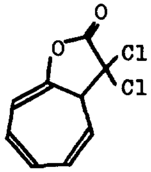
VII



VIII



IX



X

finally dehydrochlorination to V. Furthermore, the possible intermediacy of VII does not necessitate a mechanistic similarity to the isomerization of III since an alternative pathway involving dehydrochlorination with rupture of the $-\underset{\mathrm{H}}{\overset{|}{\mathrm{C}}}-\underset{\overset{\|}{\mathrm{O}}}{\overset{|}{\mathrm{C}}}$ cyclobutanone bond to give the intermediate ketene VIII followed by ring closure can occur.

Acknowledgments. We wish to thank the Petroleum Research Fund (PRF 504 G1) for support of this work as well as Dr. A.S. Kende for helpful discussions.

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