E.—A solution of hydrazone IIb (0.2 g) in concentrated sulfuric acid (4 ml) was heated on the water bath for 0.75 hr; addition of water precipitated crude III as a yellow solid (0.08 g, ∼40%).

F.—The hydrazone IIb (0.5 g) contained in a distilling flask was heated in an oil bath at 230–240° for 5–10 min and decomposed with effervescence liberating a colorless liquid (*ca.* 0.1 g) identified by its infrared spectrum as N-methylaniline. The dark red residue in the flask was warmed with 1 *N* hydrochloric acid and afforded insoluble crude III (0.1–0.2 g, ∼20–40%).

2-Phenyl-3-acetyl-4(1H)-quinolone Oxime[1] (IIc).—A mixture of 2-phenyl-3-acetyl-4(1H)-quinolone[1] (1 g), excess hydroxylamine hydrochloride (0.8 g), and sodium acetate trihydrate (1.7 g) in 60% (v/v) ethanol (40 ml) was refluxed for 15 min. Colorless crystals of the sparingly soluble oxime IIc soon commenced to separate from solution; these were filtered off from the cold mixture, washed with ethanol, dried (0.9 g, ∼85%), and found (infrared spectrum) to be contaminated with some unchanged ketone. Recrystallization from aqueous pyridine furnished colorless tiny crystals, mp 282–284°, virtually free of impurity as evidenced by the very weak absorption peak at 5.9 μ.

3-Methyl-4-phenylisoxazolo[4,5-*c*]quinoline (Ic).—The oxime IIc (0.3 g) in a test tube was heated at *ca.* 290° for 1–2 min when it melted and reacted with effervescence. The brown residue was dissolved in warm 1 *N* hydrochloric acid (charcoal) and the filtrate was made ammoniacal to deposit Ic as a colorless solid (0.15 g). Recrystallization from dilute ethanol furnished colorless woolly needles, mp 151–152°, soluble in ether and insoluble in hot dilute alkali.

Anal. Calcd for $C_{17}H_{12}N_2O$: N, 10.77; mol wt, 260. Found: N, 10.50; mol wt, 260 (mass spectrometer).

The infrared spectrum showed neither NH nor CO (amide or keto) absorption and was consistent with structure Ic. The product (0.1 g) in 2 *N* hydrochloric acid solution (5 ml) was refluxed for 20 min and was recovered unchanged (*cf.* with IVa).

2-Methyl-4-phenyloxazolo[4,5-*c*]quinoline (IVa).—The oxime IIc (0.4 g) was stirred with PPA (8 g) at ±130° for 10 min to give a yellow solution. This was poured into ice–water and the resulting pale green solution was made ammoniacal to precipitate an almost colorless solid. The latter was separated by means of warm 1 *N* sodium hydroxide into alkali-insoluble IVa (0.18 g) and an alkali-soluble "substance A" (0.1 g) which was obtained on neutralizing the alkaline filtrate with glacial acetic acid. Recrystallization of IVa from dilute ethanol furnished colorless woolly needles, mp 147–148°, soluble in ether.

Anal. Calcd for $C_{17}H_{12}N_2O$: N, 10.77; mol wt, 260. Found: N, 10.76; mol wt, 260 (mass spectrometer).

The infrared spectrum showed no NH or CO (amide or keto) absorption and differed from that of Ic.

"Substance A" after two recrystallizations from dilute ethanol was obtained as colorless woolly needles, mp 155–170°, soluble in both alkali and acid, and appeared to be a mixture; its infrared spectrum showed NH and CO (amide) absorptions and differed from that of Vb (see below).

3-Amino-2-phenyl-4(1H)-quinolone (Va).—A solution of IVa (0.2 g) in 2 *N* hydrochloric acid (10 ml) was refluxed for 30 min, cooled, and made ammoniacal to deposit a yellow solid (0.12 g, ∼70% yield, mp 200–220°). Recrystallization from dilute ethanol (charcoal) gave yellow needles, mp 243–245° (lit.[5] mp 251°) soluble in dilute alkali and mineral acids.

Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.27; H, 5.08; N, 11.86. Found: C, 75.92; H, 5.30; N, 11.95.

The solid amine Va fluoresced strongly yellow-green in ultraviolet light and its infrared spectrum showed NH absorption [3.0 μ (w), 3.3–3.6 μ (m)] and the "amide I band" at 6.12 μ (s).

3-Acetamido-2-phenyl-4(1H)-quinolone (Vb).—A solution of Va (0.2 g) in acetic anhydride (2 ml) was boiled for ∼1 min and poured into water (∼20 ml) with stirring when Vb separated as a colorless solid. This mixture was chilled and the product was filtered off and dissolved in 2 *N* sodium hydroxide; after removal of negligible insoluble impurity, the alkaline filtrate was acidified with glacial acetic acid to deposit Vb (0.15 g), colorless crystals from dilute ethanol, mp 282–284°.

Anal. Calcd for $C_{17}H_{14}N_2O_2$: N, 10.07. Found: N, 10.20.

The acetamido compound Vb (0.1 g) was stirred with PPA (4 g) at ±130° for 10 min. Ice–water was added and the mixture was made alkaline. The alkali-insoluble product (0.05 g) was filtered off and proved to be crude oxazoloquinoline IVa, colorless needles from dilute ethanol identical (mixture melting point and infrared spectrum) with those of the product IVa obtained from the oxime IIc and PPA.

3-Benzamido-2-phenyl-4(H)-quinolone (Vc).—Compound Va (0.15 g) was stirred and warmed (*ca.* 50°) with excess benzoyl chloride (0.3 ml) for 5 min. The mixture was made alkaline, negligible insoluble impurity was removed, and the filtrate was acidified with glacial acetic acid. The precipitated Vc was collected, washed free of benzoic acid with dilute ammonia, and recrystallized from ethanol to give colorless crystals (∼0.1 g), mp 290–292°. The same product was obtained also using Reverdin's[6] method.

Anal. Calcd for $C_{22}H_{16}N_2O_2$: N, 8.02. Found: 8.24.

2,4-Diphenyloxazolo[4,5-*c*]quinoline (IVb). A.—The benzamido derivative Vc (0.1 g) was stirred with PPA (1 g) at 140–145° for 10 min. Ice–water was added and the mixture was made alkaline with 2 *N* sodium hydroxide and filtered. The alkali-insoluble IVb (∼70% yield) separated from ethanol (charcoal) as colorless crystals, mp 147–148°, soluble in 2 *N* hydrochloric acid.

Anal. Calcd for $C_{22}H_{14}N_2O$: C, 81.99; H, 4.35; N, 8.70. Found: C, 81.70; H, 4.49; N, 8.87.

The infrared spectrum revealed the absence of NH and CO (amide) absorptions.

B.—A mixture of amine Va (0.1 g), excess benzoic acid (0.1 g), and PPA (3 g) was stirred at 130–160° for 20 min. Ice–water was added and the mixture was made alkaline. The alkali-insoluble product (0.1 g) was purified and proved to be identical (mixture melting point and infrared spectrum) with IVb above.

Acknowledgment.—The author is grateful to Dr. S. Eggers of the South African Council for Scientific and Industrial Research for measuring the mass spectra and helpful discussion.

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(5) C. M. Atkinson and A. R. Mattocks, *J. Chem. Soc.*, 3722 (1957).

(6) F. Reverdin, *Ber.*, **42**, 1524 (1909).

Halogenated Ketenes. II. Dibromoketene[1]

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Since Staudinger's unsuccessful attempt to prepare dichloroketene in 1913 by the thermal decomposition of the anhydride of dichloromalonic acid and diphenylketene, there has been no definitive work reported on dihalogen ketenes until rather recently.[2] Difluoroketene was reportedly prepared in 1957 by the dehalogenation of chlorodifluoroacetyl bromide.[3] Dichloroketene has been prepared in this laboratory as well as elsewhere quite recently. Stevens and co-workers prepared dichloroketene by the dehydrochlorination of dichloroacetyl chloride and treated the ketene *in situ* with cyclopentadiene.[4] Dichloroketene was synthesized in this laboratory by the dehalogenation of trichloroacetyl bromide with zinc.[5] It was reported that this ketene, unlike difluoroketene, does not distil with ether and is rather susceptible to polymerization like most low molecular weight ketenes.

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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.

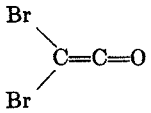
(2) H. Staudinger, E. Anthes, and H. Schneider, *Ber.* **46**, 3539 (1913).

(3) N. N. Yarovenko, S. P. Motornyi, and L. I. Kirenskaya, *Zh. Obsh. Khim.*, **27**, 2796 (1957).

(4) H. C. Stevens, D. A. Reich, D. R. Brandt, D. R. Fountain, and E. J. Gaughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965).

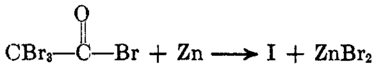
(5) Paper I: W. T. Brady, H. G. Liddell, and W. L. Vaughn, *J. Org. Chem.*, **31**, 626 (1966).

In connection with a study concerning the effect of halogen substituents on the reactivity of ketenes in nucleophilic addition reactions, it became of interest to prepare dibromoketene (I). There seems to have been no preparation or attempted preparation of this ketene in the literature.



I

The debromination of tribromoacetyl bromide with zinc activated with copper was investigated as a possible route to I since this method was so successful with dichloroketene.



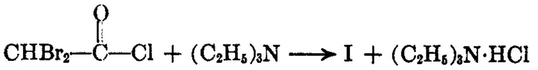
$$CBr_3—\overset{O}{\overset{\|}{C}}—Br + Zn \longrightarrow I + ZnBr_2$$

This reaction goes to completion as evidenced by the consumption of all the acid halide as well as the loss of a stoichiometric amount of zinc. This ketene, like dichloroketene, does not distil with ether as difluoroketene reportedly does. Attempts to isolate the pure material were unsuccessful. This is apparently due to polymerization of the labile material. This new ketene was shown to be present in the reaction mixture by conversion with benzylamine to N-benzyldibromoacetamide.

This new material was separated from the zinc halide and isolated in hexane. An infrared spectrum of I in hexane revealed a band at 1970 cm^{-1} which represents the stretching vibration of the ketene functionality, C=C=O. This band appears at 2160 cm^{-1} in ketene,[6] 2130 cm^{-1} in diphenylketene,[7] and 1940 cm^{-1} in dichloroketene.[5]

The stability of a dilute solution of I in hexane is comparable in stability to most low molecular weight ketenes in that the ketene is relatively stable at about 5° for several days.

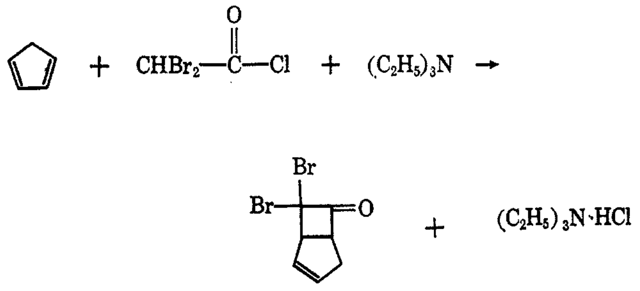
The dehydrochlorination of dibromoacetyl chloride with triethylamine was also investigated as a possible route to I since this method was also successful in the preparation of dichloroketene.



$$CHBr_2—\overset{O}{\overset{\|}{C}}—Cl + (C_2H_5)_3N \longrightarrow I + (C_2H_5)_3N{\cdot}HCl$$

The dehydrochlorination occurred as evidenced by the consumption of all the acid halide and the formation of stoichiometric amount of triethylammonium chloride. However, only a small amount of I could be detected as an amide. A polymeric material was found to predominate. Consequently, the same conclusion was reached with I that was reported with dichloroketene. Namely, I was produced but the majority of the ketene polymerized in the presence of the amine salt since tertiary amine salts are known to catalyze the polymerization of some ketenes.[8,9,10]

The formation of I by the above process was further demonstrated by the same procedure Stevens and coworkers employed with dichloroketene. That is, the dehydrochlorination was conducted at a low temperature in the presence of a reactive olefin, cyclopentadiene. This resulted in the formation of the cycloaddition product, 7,7-dibromobicyclo[3.2.0]hept-2-en-6-one (II), of I and the diene. This material was found to be unstable on standing at room temperature.



II

The structure of II was proved by a combination of elemental analysis and infrared and nmr spectra.[11] The double-bond location was assigned on the basis that the diene acts as a nucleophile which would be expected to yield II regardless of whether an ionic process or diradical mechanism was operative.[12] Also this is compatible with the orientation of the cycloadduct of cyclopentadiene and ketene,[13] dimethylketene,[14] and diphenylketene.[15]

In conclusion, I can be prepared by the two methods described. However, the debromination of tribromoacetyl bromide appears to be the method of choice as a source of this material under the conditions investigated. The dehydrochlorination of dibromoacetyl chloride as a source of I seems desirable only to react *in situ* with some species that is unreactive to the acid halide, *e.g.*, an olefin to produce a cycloaddition product.

Experimental Section

Dibromoacetyl chloride was prepared from commercially available dibromoacetic acid and thionyl chloride.[16] Bromal was oxidized with nitric acid to tribromoacetic acid by the method of Woods and Spinks.[17] The acid was then converted to tribromoacetyl bromide with phosphorus tribromide. The activation of the zinc for the dehalogenation reaction has already been described.[5]

Preparation of I by Dehalogenation.—A 16-g (0.25 mole) portion of zinc activated with copper and 100 ml of absolute ether were added to a 250-ml flask equipped with a stirrer, reflux condenser, and a dropping funnel under a nitrogen atmosphere. A solution of 18.6 g (0.0516 mole) of freshly distilled tribromoacetyl bromide in 20 ml of dry ether was added dropwise to the stirred mixture over a period of 45 min. At the conclusion of the exothermic reaction, the ether solution was separated from the unreacted zinc. The amount of zinc consumed in the reaction was 3.3 g. This dark ether solution was used as a source of I as described below.

Preparation of N-benzyldibromoacetamide from I.—The dark ethereal solution containing I was treated with an excess of benzylamine. The resulting mixture was washed with dilute hydrochloric acid and finally water. Upon drying and evapora-

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[6] D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 1005 (1946).

[7] L. G. Drayton and H. W. Thompson, *ibid.*, 1416 (1948).

[8] H. Staudinger and H. W. Klever, *Ber.*, **41**, 594 (1908).

[9] J. C. Sauer, U. S. Patent 2,238,826 (1941); *Chem. Abstr.*, **35**, 4970 (1941).

[10] D. G. Farnum, J. R. Johnson, R. E. Hess, T. B. Marshall, and B. Webster, *J. Am. Chem. Soc.*, **87**, 5191 (1965).

[11] Nmr spectrum was recorded on a Varian A-60 instrument at 60 Mc with tetramethylsilane as an internal standard.

[12] J. L. Roberts and C. M. Sharts, "*Org. Reactions*, **12**, 26 (1962).

[13] (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).

[14] T. L. Dawson and G. R. Ramage, *J. Chem. Soc.*, 3523 (1950).

[15] J. R. Lewis, G. R. Ramage, J. L. Simonsen, and W. G. Wainwright, *ibid.*, 1837 (1937).

[16] A. B. Sen and K. C. Joshi, *J. Indian Chem. Soc.*, **25**, 483 (1948).

[17] R. J. Woods and J. W. T. Spinks, *Can. J. Chem.*, **38**, 77 (1960).

tion of solvents, there was obtained 6.2 g of crude N-benzyldibromoacetamide (39% yield based on acid halide). Upon recrystallization this material had a mp of 133.5–134.5°C.

Anal. Calcd for $C_9H_9Br_2NO$: C, 35.21; H, 2.92; N, 4.56; Found: C, 35.45; H, 2.80; N, 4.57.

Isolation of I in Hexane.—An 80-ml portion of I reaction solution obtained by dehalogenation as described above containing 3.6 g of I was vigorously stirred while 100 ml of dry hexane was added dropwise under a nitrogen atmosphere. This resulted in the precipitation of the zinc halide. After the addition, the hexane solution was separated from the precipitated zinc halide with a pipet. The ether was removed by distillation to yield 100 ml of a hexane solution containing 3 g of I. This hexane solution was assayed as described previously.[5] An infrared spectrum of this solution showed the characteristic absorption of C=C=O at 1970 cm^{-1}.

The ketene could be concentrated in hexane by simply removing some of the hydrocarbon by distillation at reduced pressure. The ketene does not distil with hexane.

Preparation of I by Dehydrohalogenation.—A solution containing 11.0 g (0.047 mole) of dibromoacetyl chloride and 25 ml of dry heptane was added with stirring to 100 ml of heptane and 5.0 g (0.05 mole) of triethylamine at 0–5°. This addition was made under nitrogen atmosphere. The acid halide solution was added dropwise over a period of 30 min and stirring was continued in the cold for 1 hr. A solid separated from the reaction solution during the course of addition. This material was separated from the reaction solution by filtration and found to contain 6.5 g of triethylammonium chloride. The remaining material was black and tacky, could not be vacuum distilled, and appeared to be polymeric. The filtrate was treated with an excess of benzylamine. This solution was washed with dilute hydrochloric acid and finally water. Drying and evaporation of the solvent yielded 2 g of solid which upon recrystallization was found to be identical with N-benzyldibromoacetamide described above. This corresponds to a yield of 14% based on the acid halide.

Preparation of 7,7-dibromobicyclo[3.2.0]hept-2-en-6-one, the Cycloadduct of I and Cyclopentadiene.—A solution containing 14.5 g (0.144 mole) of triethylamine, 75 g (1.15 mole) of cyclopentadiene and 100 ml of dry hexane was cooled to 0–5° under a nitrogen atmosphere. A solution of 29.6 g (0.115 mole) of dibromoacetyl chloride in 25 ml of anhydrous hexane was added dropwise to the cooled solution over a period of 30 min. After the addition, the reaction mixture was allowed to stir for an additional 2 hr. The triethylammonium chloride which precipitated during the addition was removed by filtration. The filtrate was then concentrated on a steam bath. The residue was vacuum distilled. The high boiling portion was fractionated to yield 15.1 g at 71.5–73.5° at 0.3 mm. This corresponds to a 58% yield. This cycloadduct darkened on standing at room temperature: infrared absorption (smear), 1800 cm^{-1} (s) and 1600 cm^{-1} (w); nmr spectrum (CCl_4), pair of multiplets at 5.9 and 6.2 (–CH=CH–), multiplet at 4.3 (>CH–), and multiplet at 2.7 ppm (methylene). These peak areas were in the ratio of 1:1:1.

Anal. Calcd for $C_7H_6B_2O$: C, 31.61; H, 2.27; Br, 60.09. Found: C, 31.55; H, 2.35; Br, 59.81; mol wt, 276.

Acknowledgment.—The author is very pleased to acknowledge the laboratory assistance of James Stockton and Julius Knesek.

Peroxy Esters. *meso*-Di-*t*-butylperoxy 2,3-Diphenylsuccinate

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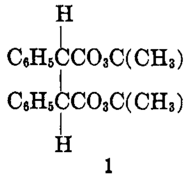
Our continuing interest in peroxy esters and their modes of decomposition has prompted us to prepare *meso*-di-*t*-butylperoxy 2,3-diphenylsuccinate (1).



$$\begin{array}{l} \quad H \\ \quad | \\ C_6H_5CCO_3C(CH_3)_3 \\ \quad | \\ C_6H_5CCO_3C(CH_3)_3 \\ \quad | \\ \quad H \end{array}$$

1

The simultaneous cleavage of two bonds during the thermal decomposition of many peroxy esters has been well established,[2] and there is evidence that in certain cases three bonds may be breaking in the rate-determining step.[3] Attempts[2,4] have been made to detect concerted four-bond cleavage, but in no case has evidence for such a reaction been found.

The rate constants for the decomposition of 1 in cumene at three temperatures are recorded in Table I. The kinetic plots showed good first-order behavior for >80% of the decomposition. There were only slight changes in the rate constants when the concentration of the peroxy ester was increased tenfold. This strongly suggests, although does not prove, that no induced decomposition is taking place and that the decomposition is truly first order. Activation parameters for this peroxy ester calculated from the rate constants are $\Delta H^* = 30$ kcal/mole and $\Delta S^* = 12$ cal/deg.

TABLE I
RATE CONSTANTS FOR THE DECOMPOSITION OF *meso*-DI-*t*-BUTYLPEROXY 2,3-DIPHENYLSUCCINATE IN CUMENE
($\Delta H^* = 30$ kcal/mole; $\Delta S^* = 12$ cal/deg mole)

Temp., °C	Concn, mole/l.	$k \times 10^{-5}$ sec^{-1}
90.0	0.009	120
90.0	0.09	124
79.9	0.009	32.9
79.9	0.09	33.6
70.1	0.009	9.83
70.1	0.09	9.89

The products from the decomposition of 1 in cumene are tabulated in Table II. *cis*-Stilbene and bibenzyl were not found among the nonvolatile products. *cis*-Stilbene is not converted to *trans*-stilbene under the conditions of the experiment.

TABLE II
PRODUCTS OF DECOMPOSITION OF *meso*-DI-*t*-BUTYLPEROXY 2,3-DIPHENYLSUCCINATE IN CUMENE AT 80°[a]

Product	Mg	mmoles	Mole/mole of peroxy ester
Carbon dioxide	82.8[b]	1.88	1.84
	83.6[c]	1.90	1.86
t-Butyl alcohol	140.8	1.92	1.88
Acetone	Trace		
trans-Stilbene	151.2	0.84	0.82
Dicumyl	169	0.50	0.49
Unidentified	120		

[a] Peroxy ester: 440 mg, 1.02 mmoles; cumene: 10 ml. [b] By volume. [c] By weight.

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(1) (a) National Science Foundation Undergraduate Research Participants (GE4169); (b) to whom inquiries should be sent.

(2) P. D. Bartlett and L. B. Gortler, *J. Am. Chem. Soc.*, **85**, 1864 (1963), and preceding papers.

(3) (a) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *ibid.*, **82**, 1762 (1960); (b) P. D. Bartlett and R. E. Pincock, *ibid.*, **82**, 1769 (1960); (c) P. D. Bartlett, B. A. Gontarev, and H. Sakurai, *ibid.*, **84**, 3101 (1962).

(4) H. Minato, Ph.D. Thesis, Harvard University, 1961.