#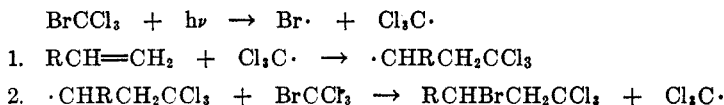 REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XIX. THE COMPARATIVE REACTIVITIES OF DOUBLE BONDS IN CYCLIC OLEFINS TOWARD FREE RADICALS

M. S. KHARASCH AND H. N. FRIEDLANDER

The photochemical free-radical chain addition of a polyhalomethane (*e.g.*, bromotrichloromethane) to olefins may be represented as follows (1):

$$BrCCl_3 + h\nu \rightarrow Br\cdot + Cl_3C\cdot$$

1. $RCH{=}CH_2 + Cl_3C\cdot \rightarrow \cdot CHRCH_2CCl_3$
2. $\cdot CHRCH_2CCl_3 + BrCCl_3 \rightarrow RCHBrCH_2CCl_3 + Cl_3C\cdot$

Steps 1 and 2 constitute the cycle, and are both critical for chain continuation. Thus, if the rate of addition of the free trichloromethyl radicals (step 1) is slow, these radicals accumulate until their concentration becomes so high that the chain is terminated by free-radical dimerization and the formation of hexachloroethane. On the other hand, if step 2 is slow, the secondary free radicals formed in step 1 may "dimerize" or add to other molecules of the olefin to yield "polymers" containing two or more molecules of olefin per molecule of bromotrichloromethane.

The relative reactivities of cyclic olefins with respect to free-radical addition. In order to compare the reactivities of olefins with respect to free-radical addition in step 1, reagents which assure the success of step 2 must be selected. It has been demonstrated[1] that bromotrichloromethane is such a reagent, for the bromine atom is easily extracted from the molecule by the secondary free radical; the product thus formed is the one-to-one adduct of the olefin and bromotrichloromethane.

The relative reactivities of two olefins in step 1 may be ascertained by allowing a one-to-one mixture of the olefins to react with a large excess of bromotrichloromethane. The reaction is allowed to proceed until about 25–50% of the olefin present has reacted, and the amount of each of the two adducts is then determined. The relative reactivities of several cyclic olefins with respect to addition of a free trichloromethyl radical (step 1) are given in Table I. The reactivity of 1-octene is taken as unity.

In all instances, the compound containing a five-membered unsaturated ring proved to be more reactive than the corresponding six-membered ring compound. Thus, cyclopentadiene is more reactive than cyclohexadiene; cyclopentene is more reactive than cyclohexene; and bicycloheptene is more reactive than bicyclooctene. The relative reactivities are thus correlated with the relative differences

[1] Kharasch, Sage, and Urry (unpublished work), have measured the relative reactivities of a series of acyclic olefins. Kharasch, Jerome, and Benca (unpublished work), have measured the relative reactivities of a series of acetylenes.

in strain between the unsaturated and the corresponding saturated ring compound. The conjugated olefins cyclopentadiene, cyclohexadiene, and indene (where the ring strain is the greatest) are more reactive than the nonconjugated olefins.

The relative reactivities of the free radicals formed in step 1 with bromotrichloromethane. In order to measure the relative reactivities of the secondary free radicals with respect to bromotrichloromethane (step 2) the reaction kinetics and the energy of activation required for this step were studied. It was observed that styrene, which adds bromotrichloromethane well at 60°, and which, at that temperature, is at least one hundred times as reactive as octene, hardly reacts at 20°. On the other hand, allyl chloride and cyclohexene give good yields of addition product even at 10°. Furthermore, styrene (which does not react with bromotrichloromethane at 20°) inhibits the reaction of allyl chloride or bicycloheptene

TABLE I

THE RELATIVE REACTIVITIES OF SOME CYCLOALKENES WITH RESPECT TO THE
ADDITION OF A FREE TRICHLOROMETHYL RADICAL

4.5	Cyclopentadiene
4.0	1,3-Cyclohexadiene
3.0	Indene
1.2	Bicyclo[2.2.1]heptene-2
1.05	Dicyclopentadiene
1.0	1-Octene
0.80	Cyclopentene
0.24	Cyclohexene
0.11	Bicyclo[2.2.2]octene-2
0.06	Butadiene sulfone

at 20°, although either one of these compounds alone reacts quite well with bromotrichloromethane at that temperature. Thus, there is a peculiar inhibition of free-radical addition by a substance which itself adds well at higher temperatures. These phenomena may be explained as follows. Styrene adds free radicals rapidly in step 1, outrunning all other competing olefins; it thereby uses up the free radicals and prevents the other olefins from capturing them. However, at low temperatures styrene does not continue the chain (step 2) at an appreciable rate. It thus effectively prevents the addition of other olefins which by themselves could readily undergo step 2. These qualitative observations indicate that there is a close connection between reaction rate and chain propagation.

The rates of the over-all reaction for several olefins at various temperatures were measured. The rate curves fit those to be expected for zero-order reactions; that is, the change in olefin concentration with time is constant. The rates are determined for the first half of the reaction period, because in the latter half there is a slight decrease in rate due to the high concentrations of the solutions used. Table II lists the rates obtained in the various over-all reactions. However, when the logarithms of the rates are plotted against the reciprocals of the absolute

temperatures in order to determine the energy of activation the curves obtained are not straight lines. Table III lists the values of the pseudo energies of activation as calculated from the rates measured in the indicated temperature intervals. Thus quantitative data concerning step 2 cannot be obtained by the method indicated.

The large variation in apparent, or pseudo activation energy (Table III) is worthy of special comment. Several alternative kinetic equations have been derived for the addition of bromotrichloromethane to olefins. The details of the kinetics so derived depend on the reactions (or reaction) chosen as the chain terminating steps. It is easily possible to obtain a kinetic equation which will agree with the experimental observation that the rate of addition of bromotri-

TABLE II

RATE OF REACTION[a] OF OLEFINS WITH BROMOTRICHLOROMETHANE

	10°	20°	30°	40°	50°
Styrene		0.004	0.09	0.16	0.17
Octene		0.07	0.59	0.70	1.11
Cyclohexene		0.07	0.11	0.14	0.19
Allyl chloride	0.03	0.08	0.14		
Bicycloheptene	0.14	0.26	0.27		

[a] Units of rate are moles/hour.

TABLE III

EXPERIMENTAL PSEUDO ACTIVATION ENERGIES IN KG. CAL. PER MOLE

	10–20°	20–30°	30–40°	40–50°
Styrene		23	4.8	0.5
Octene		16	1.4	3.4
Cyclohexene		3.5	2.2	2.7
Allyl chloride	7.2	4.2		
Bicycloheptene	4.4	0.5		

chloromethane to the olefin is independent of olefin concentration. But, the activation energy associated with such a mechanism is a linear function of the activation energies of some of the individual reactions steps (equations 1 and 2, and chain terminating steps). The calculated activation energy is thus essentially temperature independent. Since the so called "pseudo activation energy" for the addition of bromotrichloromethane to styrene decreases, over a temperature interval of thirty degrees, from 23 Kcal/mole to almost zero, any simple kinetic expression fails to account for one of the most significant features of the reaction. Perhaps, the chain terminating step for the reaction changes over the temperature interval investigated, or traces of impurities have a greater effect at some temperatures and not at others, or, perhaps, some new principle is here involved. In any event, it is clear that the apparent activation energy cannot at

present be associated with any single step or any known combination of steps in the reaction. Further, the work presented here suggests that the activation energies for all chain reactions must be carefully inspected in each individual case to determine whether or not they are strongly temperature dependent; if they are, their interpretation is questionable. In the present instance, a complete understanding of the temperature dependence of the activation energy must await further intensive investigation. ·

Properties of adducts of bromotrichloromethane and cyclic olefins. The one-to-one adducts of bromotrichloromethane and the cyclic olefins have properties similar to those of the corresponding adducts of the simple aliphatic olefins. All except those obtained from bicycloheptene, bicyclooctene, or dicyclopentadiene, when treated with bases lose hydrogen halide with relative ease. Thus, the addition compound (I) formed from butadiene sulfone can be titrated with cold alcoholic potassium hydroxide. By this treatment one molecule of hydrogen chloride and one molecule of hydrogen bromide are removed. The product is a conjugated diene (II) showing a narrow absorption peak at 2610 Å with a molecular absorption coefficient of 19,000 (2). The adduct of bromotrichloromethane and cyclohexene, 1-trichloromethyl-2-bromocyclohexane (III) when treated with cold sodium ethoxide in absolute ethyl alcohol yields a conjugated diene (IV) showing a broad absorption peak at 2500 Å with a molecular absorption coefficient of 12,000 (Figure 1). Two compounds (a solid, 32% yield, and an oil, 68% yield) were isolated from the product formed by the addition of bromotrichloromethane to 1,3-cyclohexadiene. Compounds V and VI are respectively the 1,2 and 1,4 adducts anticipated. When either the oil or the solid is titrated at 50° with alcoholic potassium hydroxide the same product, 3-dichloromethylene-6-hydroxy-cyclohexene (VIIa), is obtained. This compound has a narrow absorption peak at 2530 Å with a molecular absorption coefficient of 13,000 (Figure 1). When either the solid or the oil is titrated with cold sodium ethoxide in absolute ethyl alcohol the same alkoxy product is obtained. It is 3-dichloromethylene-6-ethoxy cyclohexene (VIIb), and is contaminated with some of the corresponding hydroxy compound (VIIa). The absorption curve of (VIIb) is practically identical with that of (VIIa); it shows a narrow peak at 2530 Å with a molecular absorption coefficient of 13,000.

Thus, the saturated cyclic adducts (I) and (III) readily lose one molecule of hydrogen bromide and one molecule of hydrogen chloride, to yield dienes. The hydrogen bromide lost contains the available hydrogen atom farthest from the trichloromethyl group. The saturated non-cyclic adducts lose only one molecule of hydrogen bromide containing the hydrogen atom nearest to the trichloromethyl group. (For example the adduct of bromotrichloromethane and 1-octene, 1,1,1-trichloro-3-bromononane, yields 1,1,1-trichlorononene-2[2] when treated with either cold sodium ethoxide or alcoholic potassium hydroxide at 50°.)

In the unsaturated cyclic adducts like V or VI where an allylic bromine is

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[2] The position of the double bond was determined by ozonization, the products being heptaldehyde and chloral.

present, the bromine atom is first replaced by the base (hydroxide or ethoxide ion) and subsequently one molecule of hydrogen chloride is removed; a hydroxy diene or ethoxy diene is thus formed.

The addition compounds of bromotrichloromethane with bicycloheptene (VIII) or bicyclooctene (IX) do not react with alcoholic potassium hydroxide at the
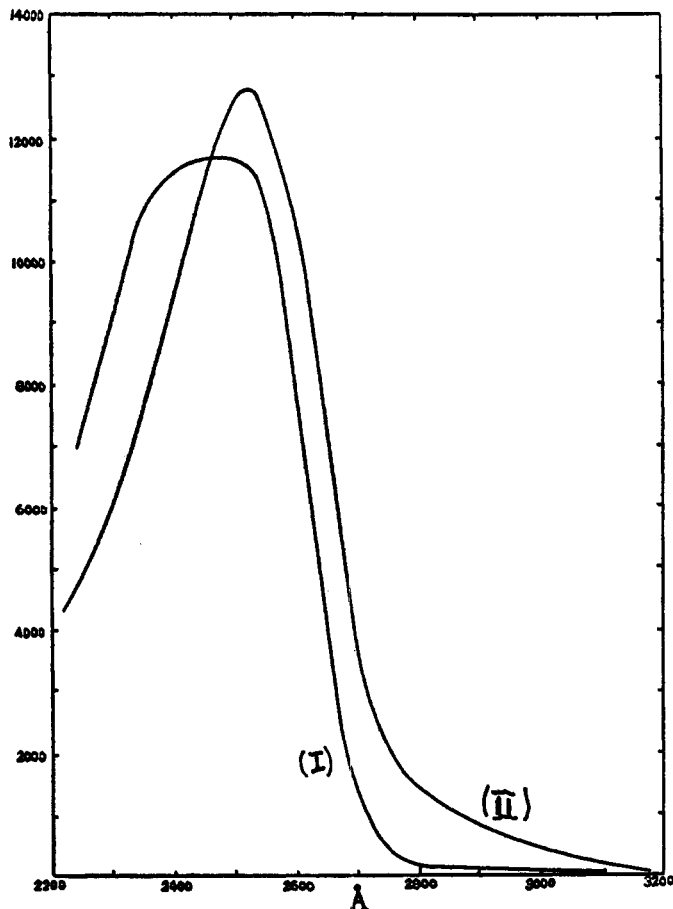

FIGURE 1. (I) 3-Dichloromethylenecyclohexene (Compound IV); (II) 6-Hydroxy-3-dichloromethylenecyclohexene (Compound VIIa).

boiling point of ethyl alcohol and are in general quite stable with respect to loss of hydrogen halide. These results are consistent with Bredt's hypothesis that a double bond at a bridge head [such as would be required by loss of hydrogen bromide from the 2 and 3 positions (IX)] is not readily formed. Loss of hydrogen bromide from the 1 and 2 positions (IX) should not readily occur in view of the behavior of the saturated cyclic adducts described above.

(I)   (II)   (III)   (IV)

(V)   (VI)   (VIIa) R = H
                (VIIb) R = C₂H₅

(VIII)   (IX)   (X)
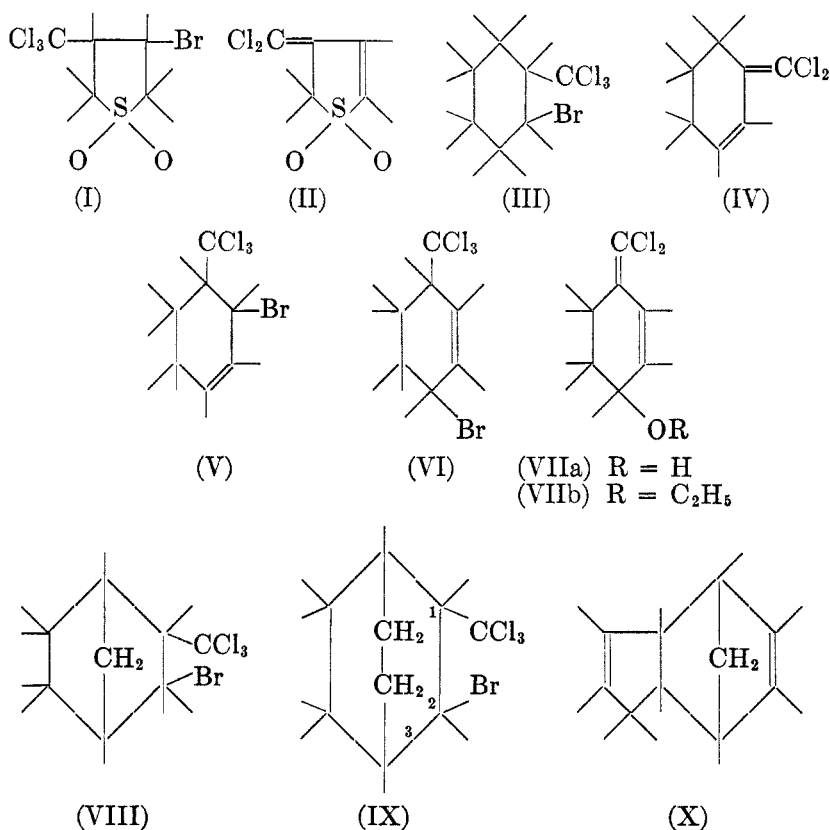
Dicyclopentadiene (X) has two double bonds; only one of them, however, adds bromotrichloromethane. The reactive one is probably the bicycloheptene double bond, for the addition compound does not react with alcoholic potassium hydroxide, and the reactivity of the olefin is closer to that of bicycloheptene than to that of cyclopentene (see Table I).

The addition compound of bromotrichloromethane and indene is 2-trichloromethyl-3-bromoindane (XI), for it is hydrolyzed by 70% sulfuric acid to indene-2-carboxylic acid.

(XI)
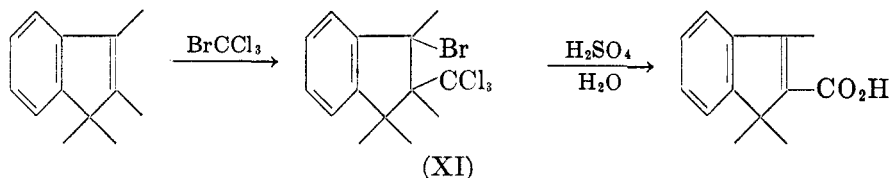
EXPERIMENTAL PART

Preparation of addition compounds. The olefin was mixed with bromotrichloromethane, and the mixture was illuminated in a glass vessel (Figure 2) containing a neon-type glass coil filled with mercury vapor. The vessel was equipped with a gas inlet tube, a sample tube, and a reflux condenser. Excess olefin and bromotrichloromethane were removed by
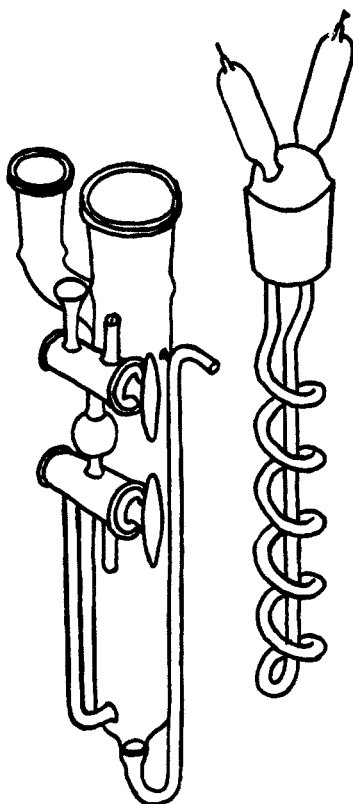
FIGURE 2

TABLE IV

ADDITION COMPOUNDS

OLEFIN	ADDITION COMPOUND (FORMULA)	B.P. °C AT 0.1 MM	n_D^{20}	SILVER EQUIVALENT	
				Calc'd	Found
Bicyclo[2.2.1]heptene-2	$C_8H_{10}BrCl_3$	70– 75	1.5538	73.1	73.2
Bicyclo[2.2.2]octene-2	$C_9H_{12}BrCl_3$	80– 85	1.5632	76.6	76.7
Cyclopentene.	$C_6H_8BrCl_3$	30– 35	1.5331	66.6	66.6
Cyclohexene.	$C_7H_{10}BrCl_3$	35– 40	1.5466	70.1	70.8
Dicyclopentadiene.	$C_{11}H_{12}BrCl_3$	110–115	1.5753	82.6	82.3
Indene.	$C_{10}H_8BrCl_3$	125–130	1.6001	78.6	79.1
Cyclopentadiene.	$C_6H_6BrCl_3$	40– 45	1.5562	66.1	67.3
1,3-Cyclohexadiene.	$\{C_7H_8BrCl_3$ (68%)	60– 65	1.5632	69.6	70.2
	$\{C_7H_8BrCl_3$ (32%)	60– 65	solid, m.p. 46°	69.6	68.9

distillation, and the residual addition compound was distilled at 0.1 mm. pressure. Table IV lists the addition compounds prepared.

Methods of competition analysis. A mixture containing 0.1 mole of each competing olefin

and 0.8 mole of bromotrichloromethane was illuminated in the apparatus hereafter described (Figure 2). The reaction was allowed to continue until about one-half of the available double bonds had reacted; this point was determined by bromide-bromate titration of samples removed from time to time. The excess bromotrichloromethane and olefins were removed by distillation, and the mixture of addition compounds was distilled at 0.1 mm. The composition of the mixture was determined by one or more of the following methods. (a) The two compounds were completely separated by distillation and the amount of each was determined gravimetrically. (b) The silver equivalent of the mixture was determined, and the quantity of each component was calculated. (c) A curve showing refractive index plotted against composition was prepared from the known mixture of the two pure addition compounds; the composition of the competition mixture was determined by the position of its refractive index on this curve. Whenever feasible all three of these methods were used. The feasibility of each method was in each instance determined by the difference between the boiling points, or the refractive indices or the silver equivalents of the two addition compounds in question.

Kinetic studies. Kinetic data were obtained by allowing 0.05 mole of the olefin to react with 0.4 mole of bromotrichloromethane in the internally irradiated apparatus hereafter described (Figure 2). The apparatus was immersed in a thermostated bath at the proper temperature. A slow stream of nitrogen was bubbled through the reaction mixture to stir it and to eliminate oxygen. A reflux condenser cooled with a mixture of carbon dioxide and acetone was used to prevent the loss of volatile olefins. The course of the reaction was followed by the bromide-bromate titration of samples withdrawn at regular intervals.

Dehydrohalogenation of addition compounds. 1-Trichloromethyl-3-bromocyclohexane (III) was heated with two molecular equivalents of sodium ethoxide in absolute ethanol for twenty-four hours at 20°. The reaction mixture was decomposed with water, and the aqueous solution was extracted with ether and benzene. The ether-benzene solution was dried, the solvent was removed, and the remaining oil was distilled at reduced pressure. A center cut was taken. The ultraviolet absorption spectrum of this material dissolved in isopropanol was determined with the aid of a Beckman type D spectrophotometer (see Figure 1). The product proved to be 3-dichloromethylenecyclohexene (IV).

Anal. Calc'd for $C_7H_8Cl_2$: Cl, 43.5. Found: Cl, 43.3, 43.1.

A portion (0.2 mole) either of the solid or the liquid addition compound obtained from 1,3-cyclohexadiene was treated for two hours at 50° with two molecular equivalents of 0.7 N alcoholic potassium hydroxide. The reaction mixture was first filtered to remove precipitated bromide and chloride and then added to water. The aqueous solution was extracted with ether and ligroin. The ether-ligroin solution was dried over sodium sulfate; after the solvent was removed the remaining oil was distilled at 0.1 mm. A center cut was taken. The ultraviolet absorption spectrum of this material dissolved in 2,2,4-trimethylpentane (isooctane) was determined with the aid of a Beckman type D spectrophotometer (see Figure 1). The product proved to be 3-dichloromethylene-6-hydroxycyclohexene (VIIa), n_D^{20} 1.5528.

Anal. Calc'd for $C_7H_8Cl_2O$: C, 47.0; H, 4.51; Cl, 39.6.
          Found: C, 47.3, 47.9; H, 4.85, 5.21; Cl, 39.6, 39.2, 38.6.

Both the solid and liquid addition compounds of 1,3-cyclohexadiene were mixed with two molecular equivalents of sodium ethoxide in ethyl alcohol and allowed to stand at room temperature overnight. The precipitated salts were removed by filtration; the filtrate was diluted with water, and the aqueous solution was extracted with ligroin. The ligroin was dried over sodium sulfate; after the solvent had been removed, the remaining oil was distilled at 6 mm. pressure. The principal fraction (b.p. 78–80°, n_D^{20} 1.5336) is 3-dichloromethylene-6-ethoxycyclohexene (VIIb) containing about 25% of the 6-hydroxy compound (VIIa).

Anal. Calc'd for $C_9H_{12}Cl_2O$: C, 52.3; H, 5.81; Cl, 34.7.
          Found: C, 50.95, 51.19; H, 5.83, 5.60; Cl, 36.7, 37.0, 36.4.

The ultraviolet absorption spectrum of this material dissolved in isooctane was determined with the aid of a Beckman type D spectrophotometer.

The addition compounds of bromotrichloromethane with bicyclo[2.2.1]heptene-2, (VIII) dicyclopentadiene (X) and bicyclo[2.2.2]octene-2 (IX) do not react when treated for 6 hours at 50° with 0.7 N potassium hydroxide in absolute ethanol.

Identification of bromotrichloromethane—indene addition product (2-trichloromethyl-3-bromoindane). Three grams of the addition compound was refluxed for 40 min. with 3.2 ml. of concentrated sulfuric acid and 2.5 ml. of water. The reaction mixture was diluted with water and ice, and extracted with benzene. The benzene extract was first washed with dilute alkali; then the alkaline solution was acidified. The white solid which precipitated at this point was crystallized from benzene; it melted at 234–235°. The value given in the literature for the melting point of indene-2-carboxylic acid is 234°. Indene-3-carboxylic acid melts at 161°.

Irradiation apparatus (Figure 2). The irradiation apparatus used in this work consisted of a reaction tube 30 mm. in diameter and approximately 200 mm. long. It had a standard taper 34/45 joint at the top and at the bottom a sintered disc through which gas was passed during the reaction. Through an outlet near the bottom of the reactor, 1-ml. samples were withdrawn by means of an arrangement of stopcocks and a 1-ml. bulb. A reflux condenser was attached to the apparatus by means of a 19/38 standard taper ground joint entering the reaction tube near the top. The lamp was fitted into the reactor tube by means of the 34/45 standard taper ground joint. This lamp was of the cold-electrode type with a filling of argon and mercury. The tubing of the coil was 6 mm. O.D. The lamp was operated from a 6000 volt, 20 milliampere transformer.

SUMMARY

1. The relative reactivities of cyclic olefins with respect to the addition of free trichloromethyl radicals have been studied. Compounds containing five-membered unsaturated rings are more reactive than the corresponding six-membered ring compounds.

2. The kinetics of the addition of bromotrichloromethane to olefins was studied.

3. The preparations of some conjugated cyclic olefin derivatives from bromotrichloromethane adducts are described.

CHICAGO 37, ILL.

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