methanol was evaporated directly and the remaining oil taken up in ether, washed with 10% aqueous sodium carbonate and water, and then dried with anhydrous magnesium sulphate. Fractionation through an efficient column (about ten theoretical plates) yielded compounds XI and XII.

In the preparation of trialkylacetic esters the reaction mixture was first treated with potassium hydroxide (0.5 mole) and water (10–15 ml.) at reflux temperature for 3 hr. in order to remove the by-products resulting from the disproportionation of the intermediate carbethoxyalkyl radicals. As the by-products are esters with a single α-alkyl substituent they are hydrolyzed by this treatment, whereas the trialkylacetic ester is left unchanged. The cooled solution was poured into 2 l. of water and the organic layer was taken up in petroleum ether (b.p. 30–50°). The combined extracts were washed twice with water, dried with Drierite, the petroleum ether distilled, and the residual oil fractionated through a ten-plate column, yielding compounds I–X.

Preparation of Trialkylacetic Acids.—The trialkylacetic esters (0.1 mole) (or 2,2-dialkylglutaric ester, 0.05 mole) was refluxed for 24 hr. with a mixture of potassium hydroxide (0.3 mole) and ethylene glycol (60 ml.) or ethanol (40 ml.). The use of ethanol was found to be more satisfactory since the esters were easily soluble in this medium. The reaction mixture was poured into water and the alkaline solution was extracted once with ether in order to remove traces of unchanged ester. After acidification with concentrated hydrochloric acid the organic layer was taken up in ether, the ether solution washed with water, and ether and traces of water were evaporated *in vacuo* in a rotating-film evaporator. Finally the trialkylacetic acid (or 2,2-dialkylglutaric acid) was purified by distillation at reduced pressure or recrystallization from an appropriate solvent. During vacuum distillation of the trialkylacetic acids there always occurred considerable foaming, which made it advisable to use a relatively large distilling flask.

Solid derivatives of the trialkylacetic acids were prepared according to conventional procedures and all melting points were determined in a Leitz melting point microscope.

Ionization Constants.—These were determined according to the directions given by Hammond and Hogle[19] with an automatically recording titration apparatus from Radiometer, Copenhagen, Denmark. They were reproducible to within ±0.02 pH-unit.

Acknowledgment.—The author is grateful to Draco, Lunds Farmacevtiska AB, for their kind support of this work.

Addition of Ethyl Tribromoacetate to Butadiene Induced by Ultraviolet Radiation

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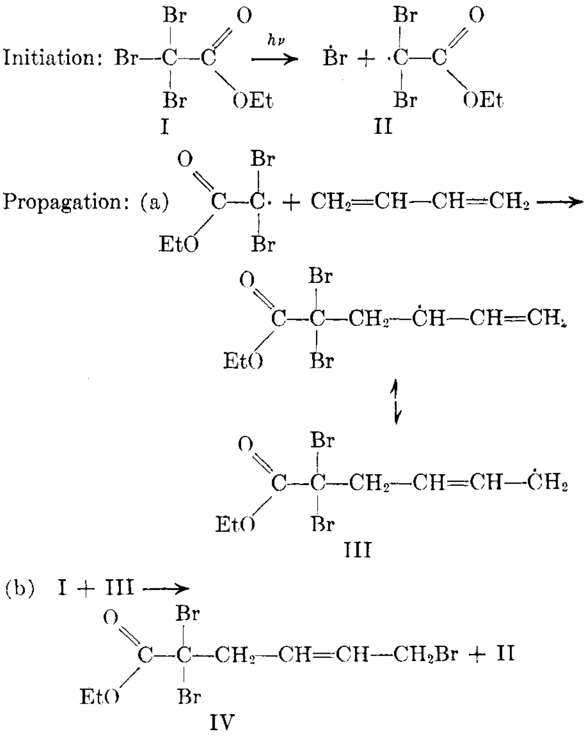
During the course of an investigation of the x-ray induced addition of halogenated esters of acetic acid to 1,3-butadiene, for preparing possible intermediates to be used in the synthesis of lysine, it has been found that ethyl tribromoacetate adds readily to butadiene to give high yields of 1:1 adduct. Ethyl dibromoacetate adds less readily.

While preparing mixtures for a kinetic study in which the disappearance of butadiene was to be followed by optical absorption in the near infrared,[1] it was discovered that the reaction occurred without X-irradiation. However, when ethyl tribromoacetate and 1,3-butadiene were mixed in the dark no reaction took place. It was also noted that the total radiation emitted by the light source of the Cary Model 14 spectrophotometer caused the reaction to occur. When a yellow filter was placed in the light beam to remove violet and ultraviolet radiation, no reaction occurred. (When working in the near infrared with this instrument, the sample is placed in the light beam before the beam encounters the dispersing unit.) Thus the reaction between the components was shown to be photochemical in nature and, accordingly, the ultraviolet-initiated reaction was investigated.

Although butadiene does not absorb in the near ultraviolet, ethyl tribromoacetate absorbs at wave lengths as high as 400 mμ, and absorption is very strong below ~352 mμ, which would explain the photochemical initiation of the reaction.

A great amount of work in the free radical addition of polyhalogenated compounds to unsaturated systems has been reported by Kharsch and others and summarized by Walling.[2] The reaction can be represented by the following:



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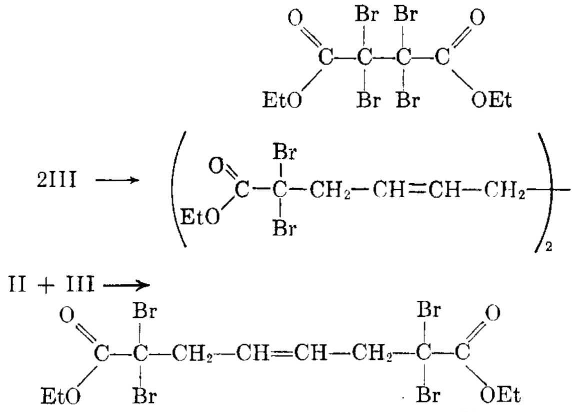
[1] Catherine S. Hsia Chen and Robert F. Stamm, submitted to *J. Org. Chem.*

[2] C. Walling, "Free Radicals in Solution," John Wiley and Sons, New York, 1957, Chap. 6.

Termination: (a) Bimolecular: 2II ⟶



(b) Unimolecular: Formation of stable radicals (degradative chain transfer)

The product obtained was found to be *trans*-ethyl 2,2′,6-tribromohexene-4-oate-1 (IV), resulting from 1,4-addition. The infrared spectrum of the product shows a C=O peak at 1733 and shoulder at 1750 cm.$^{-1}$; a *trans*-disubstituted double bond peak at 970 cm.$^{-1}$; no strong band between 850 and 650 cm.$^{-1}$ indicating the absence of *cis* double bond; and no strong band at 920 cm.$^{-1}$ indicating the absence of terminal $CH=CH_2$; the rest of the spectrum is reasonable for the proposed structure.

Some kinetic studies have been undertaken. Quantum yields at 3650 Å. and 3341 Å. under several experimental conditions were obtained. These two wave lengths were chosen because they are easily isolated by filter combinations. Also, the ultraviolet absorption spectrum of ethyl tribromoacetate showed appreciable absorption at 3650 Å. and strong absorption at 3341 Å., and it has been shown that light energy at these wave lengths causes reaction. Neither butadiene nor the product dissolved in ethyl tribromoacetate causes any change in the ultraviolet absorption curve of ethyl tribromoacetate. The results of the rate study are recorded in Table I, and the rate plots are represented in Fig. 1.

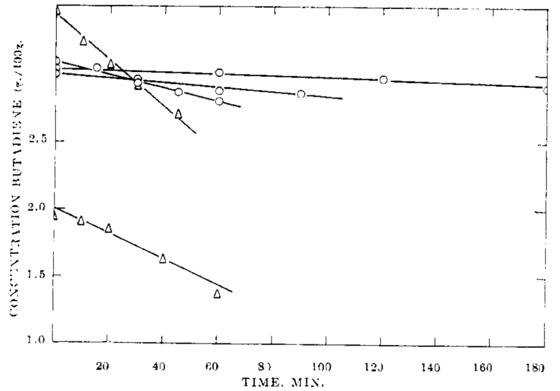


Fig. 1.—Rate plots. Disappearance of butadiene *vs.* time.

△ 3650 Å ○ 3341 Å

Table I

Addition of Ethyl Tribromoacetate to 1,3-Butadiene Initiated by Ultraviolet Radiation at 25°C.

Mole ratio, ETBA butadiene	Wave length Å.	Intensity, ergs absorbed/min.	Rate: $-\frac{d[\text{buta}]}{dt}$ moles/kg./min.	Quantum yield
4.62:1	3650	2.09×10^5	3.05×10^{-3}	297
8.27:1	3650	1.93×10^5	1.85×10^{-3}	191
5.35:1	3341	3.42×10^4	9.34×10^{-4}	603
5.06:1	3341	1.53×10^4	3.72×10^{-4}	539
5.09:1	3341	5.95×10^3	2.16×10^{-4}	803

Based on these results, the following conclusions can be made. (1) Quantum yields of the order found indicate a chain reaction of fairly high efficiency. (2) The straight line plots of the concentration of butadiene *vs.* time (Fig. 1) indicate that the reactions are zero order in butadiene. However, the rate is dependent on the concentration of ethyltribromoacetate as shown in the results represented in rows 1 and 2 in Table I where different initial concentrations were employed while other conditions were held essentially constant. (3) When the rates and quantum yields are plotted against the intensity of light (log-log basis) using the data obtained for 3341 Å. (rows 3–5, Table I), the dependence of rate and quantum yield on intensity of light are obtained as the slopes of the least squares' lines as represented by the open and solid circles in Fig. 2. It is seen that: rate α (intensity)$^{0.83}$; quantum yield α (intensity)$^{-0.17}$.

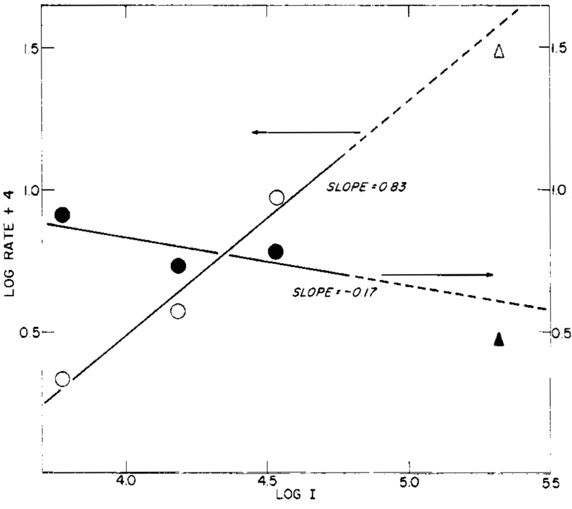


Fig. 2.—Intensity dependence of rate and quantum yield.

At wave length 3341 Å.: ○ rate ● quantum yield
At wave length 3650 Å.: △ rate ▲ quantum yield

For reactions obeying the laws of homogeneous reaction kinetics, the following should be true: For unimolecular termination: rate α (Intensity)^1; quantum yield α (intensity)^0. For bimolecular termination: rate α (intensity)$^{0.5}$; quantum yield α (intensity)$^{-0.5}$.

It is apparent then that in the above reaction the termination of the kinetic chains is a mixture of bimolecular radical-radical combination and unimolecular degradative chain transfer. (4) The triangles in Fig. 2 represent the results obtained by employing 3650Å under comparable experimental conditions (row 1, Table I). It is seen that the points lie close to the respective lines extrapolated from the results for 3341 Å. This observation leads one to assume that there is no appreciable difference in efficiency between the two wave lengths.

Experimental

Materials Used.—Butadiene was the research grade of Phillip's Petroleum Company. Ethyl tribromoacetate (ETBA) was prepared by esterification of tribromoacetic acid following the procedure of Broche.[3] Tribromoacetic acid was prepared by the method described by Schaeffer.[4]

Ethyl 2,2′,6-Tribromohexene-4-oate-1.—When butadiene was mixed with excess ETBA (1 mole of butadiene to 2 moles or greater of ETBA) at room temperature under the influence of daylight, quantitative conversion of butadiene to ethyl 2,2′,6-tribromohexene-4-oate-1 was obtained in several hours. The product was separated from ETBA by distillation using a 1-in. Vigreux column. After removal of ETBA, ethyl 2,2′,6-tribromohexene-4-oate-1 was obtained as a pale yellow liquid; b.p. 90–93°/0.04 mm; $n^{25}\text{D}$ 1.5472.

Anal. Calcd. for $C_8H_{11}O_2Br_3$: C, 23.56; H, 2.93; Br, 63.27; O, 8.44. Found: C, 24.91; H, 2.90; Br, 62.48.

Kinetic Runs.—The source for both monochromatic light at 3650 Å. and 3341 Å. was an 85-watt AH-3 mercury lamp. A simple shutter permitted light to enter the box containing sample and filters, as desired. A black cloth was placed over the entire set up (except source) to exclude any outside light. The filter system to isolate the 3650 Å. group of emission lines consisted of Corning filters numbers 7380 (2 mm.) and 5860 (5 mm.) The filter system to isolate the 3341 Å. emission line, taken from Kasha,[5] consisted of Corning filter number 5970 (5 mm.), a solution of 12.8 g. of naphthalene/l. of iso-octane in a 10-mm. quartz cell, and a solution of 100 g. of nickel sulfate hexahydrate/l. water in a 50-mm. quartz cell.

The reactions were carried out in a 20-mm. quartz cell with a silicon rubber stopper which prevented the escape of butadiene. A typical run was begun by weighing the desired amount of ETBA into the tared cell. Uuder a black cloth, butadiene, twice distilled, was bubbled into the cell *via* a glass capillary tube until the cell was filled (3-ml. capacity). The cell was then reweighed on an analytical balance protected completely from light by a black cloth except the door which was covered by an orange sheet of plastic to permit visibility. Initial absorption data for the known concentration of butadiene in ETBA were obtained at 1.63 μ on the Cary 14 spectrophotometer by scanning the region from 1.66–1.59 μ *vs.* ETBA in a 20-mm. cell in the reference beam, with yellow filters in both beams to exclude ultraviolet light. The sample cell, protected from extraneous light during all manipulations, was then placed in the sample holder of the apparatus and exposed to the monochromatic light for time intervals. After each interval the absorption of butadiene at 1.63 μ was determined. The reactions were carried out in a constant temperature room maintained at 25.0 ± 0.5°. The reactions were followed until 10–20% of the butadiene had disappeared.

The optical densities (absorbances) at 1.63 μ were corrected for background, and the concentration of butadiene was calculated from the linear relationship between absorbance and concentration (determined by least squares analysis of the straight line plot of concentration of butadiene in standard solution *vs.* $A_{1.63\,\mu}$).

The ferrioxalate actinometer solution was used for determining the incident energy of the two wave lengths after each run, following the standard procedure.[6] Different intensities were obtained by inserting wire screens of varying absorbancy between the light source and the sample. The number of quanta absorbed was determined by utilizing absorption coefficients at appropriate wave lengths obtained from the ultraviolet absorption spectrum of the ETBA after ascertaining that the presence of the butadiene and the product did not alter the absorption coefficients.

Acknowledgment.—The authors wish to express their gratitude to Dr. R. F. Stamm for his guidance and encouragement, to Dr. Norma Searle for her assistance in carrying out the ultraviolet kinetic study, and to Mr. Norman Colthup for his assistance in interpreting the infrared spectra.

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Substituted γ-Lactones. IX.[1] Synthesis of Some Substituted 3-Arylidenephthalides[2]

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In a previous paper[1] the alkali-catalyzed aldol-type condensation between phthalide and aromatic aldehydes was described. Contrary to the literature[3] it was found that condensation occurred, and even more interestingly, under certain conditions the corresponding aldols were formed in high yields and could be isolated and characterized. It has been known for some time[4] that 6-nitrophthalide condenses with aromatic aldehydes to yield 3-arylidene-6-nitrophthalides. In the light of our findings and the fact that only a few aldehydes with electron-donating substituents were employed for the condensation with 6-nitrophthalide, it was decided to investigate further this reaction. Consequently, a number of benzaldehydes substituted with activating as well as deactivating groups were subjected to condensation with 6-nitrophthalide.

All of the aldehydes which were employed, condensed with 6-nitrophthalide; however, no aldols were found. The results given in Table I

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[1] Paper VIII, H. Zimmer and R. D. Barry, *J. Org. Chem.*, **27**, 1602 (1962).

[2] Taken in part from the Ph.D. thesis of R. D. Barry, University of Cincinnati, 1960; Chattanooga Medicine Co. Fellow, 1957–1959; Ethyl Corp. Fellow 1959–1960. Present address: Organic Research Laboratories, Department of Obstetrics and Gynecology, University Hospital, The Ohio State University, Columbus, Ohio.

[3] See ref. 1 for pertinent references.

[4] W. Borsche, K. Diacont, and H. Hanau, *Ber.*, **67**, 675 (1934).