viously described. The value of k_2 was calculated from the equation, $k = k_1 + k_2(\text{OH})$, using the k_1 value obtained in neutral solution.

Time, hr.	Reacted, %	$k = k_1 + k_2(\text{OH}^-)$	k_2, (l. mole^{-1} hr.$^{-1}$)
0.5	15.2	0.32	0.11
1.5	37.0	.31	.11
3.0	55.5	.28	.09

Acid Solution.—*o*-Chloromethylsulfonylbenzoic acid (0.469 g., 0.002 mole) was dissolved in 12.5 ml. of water in a tube, and the tube was immersed in boiling water. Samples were titrated for chloride as previously described.

Time, hr.	Reacted, %	k, hr.$^{-1}$
3.0	8.3	0.029
4.5	11.6	.028

Decomposition of *p*-Chloromethylsulfonylbenzoic Acid in Neutral and Basic Solutions. Neutral Solutions.—*p*-Chloromethylsulfonylbenzoic acid was neutralized with sodium bicarbonate as described above for *o*-chloromethylsulfonylbenzoic acid. After 20 hr. at 100° no detectable amount of chloride had been released.

Basic Solution.—*p*-Chloromethylsulfonylbenzoic acid was heated in 2 *N* sodium hydroxide solution as described above for *o*-chloromethylsulfonylbenzoic acid.

Time, hr.	Reacted, %	k, l. mole^{-1} hr.$^{-1}$
1.1	3.3	0.016
6.3	19.0	.018
18.6	48.4	.019

The solution readily decolorized a 2% potassium permanganate solution. On warming with 30% hydrogen peroxide and treatment with S-benzylthiuronium chloride, a small amount (7%) of the S-benzylthiuronium salt of *p*-sulfobenzoic acid, m.p. 213–214°, was obtained; lit.[9] m.p. 212.6–214.4°. The melting point of a mixture with an authentic sample was undepressed.

Attempted Reaction of *p*-Methylsulfonylbenzoic Acid with Sodium Hydroxide Solution.—Two grams of *p*-methylsulfonylbenzoic acid was heated under reflux in a stream of nitrogen with 25 ml. of 2 *N* sodium hydroxide solution for 48 hr. The solution did not decolorize 2% potassium permanganate. Acidification and recrystallization of the precipitate from glacial acetic acid yielded 1.8 g. (90%) of the starting material.

Attempted Reaction of *o*-Methylsulfonylbenzoic Acid with Sodium Hydroxide Solution.—Two grams of *o*-methylsulfonylbenzoic acid was heated under reflux in a stream of nitrogen with 25 ml. of 2 *N* sodium hydroxide for 4 hr. The solution did not decolorize 2% potassium permanganate. Acidification, extraction with benzene and recrystallization from benzene–petroleum ether yielded 1.3 g. (65%) of starting material.

Acidity Constant Measurements.[6]—The acidity constants were determined with a Beckman model G *p*H meter according to the method described previously.[14]

Pertinent data are summarized in Table I.

TABLE I

C = concn., mole/liter C	C_b	C_a	*p*H (av.)	pK_a	pK_a (av.)
		o-Chloromethylsulfonylbenzoic acid			
0.01435	0.00368	0.01067	2.46	2.46	
.01769	.00735	.00974	2.51	2.33	
.01691	.01011	.00680	2.74	2.36	
.01590	.00368	.01192	2.38	2.36	2.38
		p-Chloromethylsulfonylbenzoic acid			
0.003232	0.000735	0.002497	3.27	3.46	
.004112	.001618	.002495	3.40	3.42	
.004276	.002572	.001704	3.70	3.44	3.44

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[14] See F. G. Bordwell and P. J. Boutan, THIS JOURNAL, **78**, 854 (1956), and previous papers cited therein.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Free-Radical, Chain Reactions of Diazomethane with Polybromo- and Polyiodomethanes

BY W. H. URRY, J. R. EISZNER AND J. W. WILT

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A high quantum yield (298 at 0–2°) confirms previous suggestions that the photochemical reaction of diazomethane with carbon tetrachloride to give pentaerythrityl chloride and nitrogen is a free-radical, chain reaction. The more rapid chain reactions of diazomethane with polybromo- or polyiodomethanes give halide products of a different type—dibromo- or diiodomethane and vinyl or vinylidene bromides or iodides. β-Elimination of a bromine or iodine atom from an intermediate free radical is postulated.

The reactions of diazomethane with polybromo- or polyiodomethanes give the respective dihalomethanes and vinyl or vinylidene halides as well as nitrogen and higher boiling telomeric products of secondary reactions of the polyhalomethanes with the haloethylenes. In our initial studies, the following reactions were observed when gaseous diazomethane was passed into irradiated solutions of the polyhalomethane (yields based upon diazomethane in parentheses; theoretical yield of each halide is 50%)

$$\text{CBr}_4 + 2\text{CH}_2\text{N}_2 \longrightarrow \text{CH}_2\text{Br}_2(25\%) + \text{CH}_2{=}\text{CBr}_2(25\%) + 2\text{N}_2 \quad (1)$$

$$\text{CHI}_3 + 2\text{CH}_2\text{N}_2 \longrightarrow \text{CH}_2\text{I}_2(45\%) + \text{CH}_2{=}\text{CHI}(27\%) + 2\text{N}_2 \quad (2)$$

$$\text{CHBr}_3 + 2\text{CH}_2\text{N}_2 \longrightarrow \text{CH}_2\text{Br}_2(15\%) + \text{CH}_2{=}\text{CHBr-telomer} + 2\text{N}_2 \quad (3)$$

Later experiments (with CBr_2Cl_2) showed, however, that these reactions occur when diazomethane is added to these halides in ordinary room light (at 0–35°) with no additional irradiation.

These reactions differ in two significant ways from the previously studied reactions[1] of diazomethane with polyhalomethanes (CCl_4, BrCCl_3 and CHCl_3) and α-haloesters ($\text{Cl}_3\text{CCOOCH}_3$ and $\text{BrCH}_2\text{COOCH}_3$): (1) they are much faster (reaction occurred with mixing), and (2) the products of the latter reactions are neopentyl derivatives[2]

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[1] W. H. Urry and J. R. Eiszner, THIS JOURNAL, **73**, 2977 (1951); **74**, 5822 (1952).

[2] Recent work has shown that products formed by reactions of free radical intermediates with the polyhalomethanes are also formed. For example, when diazomethane was passed into bromotrichloromethane at 0° over a period of 90 minutes, the products 1-bromo-1,1,2-trichloroethane (0.8%), 2-bromo-1,2,3-trichloropropane (17%), 2-bromo-2-chloromethyl-1,3-dichloropropane (16%), and 2-bromomethyl-2-chloromethyl-1,3-dichloropropane (15%, yields based upon diazomethane) were obtained. Such products are formed in largest amounts with the most reactive polyhalomethanes and when the concentration of diazomethane in the reaction mixture is kept low; W. H. Urry and N. Bilow, unpublished work.

(except with $BrCH_2COOCH_3$) in which in general a methylene group is interposed between each halogen atom and the carbon to which it was attached ($CCl_4 \rightarrow C(CH_2Cl)_4$; $Cl_3CCOOCH_3 \rightarrow (ClCH_2)_3CCOOCH_3$; $BrCH_2COOCH_3 \rightarrow BrCH_2CH_2COOCH_3$). These differences may be attributed to (1) the greater reactivity of organic bromides and iodides to free radical attack which results in greater chain length and (2) the tendency for intermediate free β-bromo- or β-iodoethyl radicals to undergo a β-elimination of a bromine or iodine atom rather than the 1,2-shift of chlorine postulated in the earlier study for free β-chloroethyl radicals. In detail the mechanism proposed for the reaction of diazomethane with CBr_4 is

$$CH_2N_2 \longrightarrow :CH_2 + N_2 \qquad (1)$$

$$:CH_2 + CBr_4 \longrightarrow BrCH_2\cdot + \cdot CBr_3 \qquad (2)$$

$$\text{and } BrCH_2\cdot + CBr_4 \longrightarrow BrCH_2Br + \cdot CBr_3$$

$$\cdot CBr_3 + CH_2N_2 \longrightarrow \cdot CH_2CBr_3 + N_2 \qquad (3)$$

$$\cdot CH_2CBr_3 \longrightarrow CH_2{=}CBr_2 + \cdot Br \qquad (4)$$

$$\text{or } \cdot CH_2CBr_3 + CH_2N_2 \longrightarrow CH_2{=}CBr_2 + \cdot CH_2Br + N_2 \qquad (4a)$$

$$\cdot Br + CH_2N_2 \longrightarrow BrCH_2\cdot + N_2 \qquad (5)$$

$$\cdot CH_2Br + CBr_4 \longrightarrow CH_2Br_2 + \cdot CBr_3 \qquad (6)$$

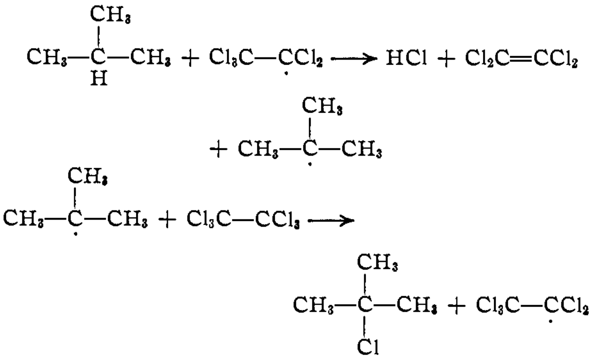
This mechanism permitted prediction of products to be expected in the reaction of diazomethane with dibromodichloromethane. Since carbon tetrachloride and bromotrichloromethane react to give 1,3-dichloro-2,2-bis-(chloromethyl)-propane and 1,3-dichloro-2-bromomethyl-2-chloromethylpropane, respectively, and carbon tetrabromide reacts as above, it was of interest to determine with which chlorobromomethane in the series (CCl_4, $BrCCl_3$, Br_2CCl_2, Br_3CCl, CBr_4) the transition in mechanism occurs. Dibromodichloromethane should react by the elimination mechanism since it is the first member of the series to provide an intermediate free radical ($\cdot CH_2CCl_2Br$) with a bromine atom attached to the β-carbon atom. Accordingly, it was found that its reaction with diazomethane gave dibromomethane (21%) and 1,1-dichloroethylene (12%). A careful search was made for 1,3-dibromo-2,2-bis-(chloromethyl)-propane but none was found.

A free-radical, chain mechanism for the reactions of diazomethane with polychloromethanes and α-haloesters was suggested[1] by the experimental evidence: (1) reaction of zero order in diazomethane at constant temperature and light intensity, (2) light-initiation of the reaction, (3) inhibition by diphenylamine and (4) only organic halides which undergo free-radical, chain addition to olefins give this reaction. The observation that the quantum yield of nitrogen in the reaction of diazomethane with carbon tetrachloride is about 300 (at 0–2°, see Experimental Part) further supports this theory. Present evidence suggests that the reactions with polybromo- and polyiodomethanes are even longer in chain length. Immediate reaction occurs upon mixing the reactants (see Experimental Part—the CH_2N_2–CBr_2Cl_2 reaction) in diffuse daylight (0–35°). In contrast diazomethane reacts slowly with carbon tetrachloride in the dark[1] (approximately 0.7% reaction in 35 minutes at 0°). This dark reaction may be attributed to initiation by a slow thermal decomposition of diazomethane, and a measurable amount of nitrogen results from the ensuing chain reaction. Presumably, this slow thermal decomposition plus a small amount of photochemical initiation by the diffuse light are sufficient to induce (reactions 1 and 2) the fast reactions of diazomethane with the polybromo- and polyiodomethanes.

Photochemical initiation is apparently not necessary for these reactions in the temperature range studied (0–35°). A chain mechanism is confirmed, however, by the observed inhibition by diphenylamine of the reaction of diazomethane with carbon tetrabromide. An induction period of 30 minutes was observed, and the reaction continued at a declining rate for two hours after its start.

Mechanisms involving β-elimination of halogen from an intermediate free radical have been postulated previously for a number of reactions. Examples are the free-radical dimerization of methallyl chloride[3] and the peroxide-induced reactions of bromotrichloromethane with allyl bromide,[4,5] of alkanes and alkylbenzenes with polychloroethylenes,[6] and of hexachloroethane with alkanes.[7] Opinions differ as to the details of the β-halogen removal. It has been represented as a one-step transfer of the β-halogen atom from the free radical to a reactant molecule (as in the mechanism above—reaction 4a), or a two-step sequence to the same products—elimination of a free halogen atom which then reacts (reactions 4 and 5 above). The present work, in common with most previous investigations, provides no evidence to indicate which is the preferred course.

In one previous study[7] there is an indication that a free halogen atom is not an intermediate. Schmerling and West[7] found that the *t*-butyl peroxide-induced reaction of 2-methylpropane with hexachloroethane gave 2-chloro-2-methylpropane and tetrachloroethylene in quantitative yields. This result suggests that the chain propagating reactions are



$$(CH_3)_3CH + Cl_3C\text{—}\dot{C}Cl_2 \longrightarrow HCl + Cl_2C{=}CCl_2 + (CH_3)_3\dot{C}$$

$$(CH_3)_3\dot{C} + Cl_3C\text{—}CCl_3 \longrightarrow (CH_3)_3CCl + Cl_3C\text{—}\dot{C}Cl_2$$

The alternative mechanism—elimination from the free pentachloroethyl radical of a free chlorine atom and its subsequent attack upon 2-methylpropane—

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[3] K. E. Wilzbach, F. R. Mayo and R. Van Meter, THIS JOURNAL, **70**, 4069 (1948).

[4] M. S. Kharasch and M. Sage, *J. Org. Chem.*, **14**, 79 (1949).

[5] M. S. Kharasch and G. Buchi, *ibid.*, **14**, 84 (1949).

[6] L. Schmerling and J. P. West, THIS JOURNAL, **71**, 2015 (1949), and **75**, 6216 (1953).

[7] J. P. West and L. Schmerling, *ibid.*, **72**, 3525 (1950).

should have given some 1-chloro-2-methylpropane. Two reactions which involve attack by free chlorine atoms on this hydrocarbon have been investigated. Its photochemical liquid-phase chlorination[8] at 100° gave 1-chloro-2-methylpropane (75%) and 2-chloro-2-methylpropane (25%), and its photochemical reaction[9] with sulfur dioxide and chlorine in carbon tetrachloride at 25° gave only 2-methylpropane sulfonyl chloride (90%).

The previous observation that the photochemical reaction of diazomethane with methyl trichloroacetate gives methyl tris-(chloromethyl)-acetate (60%) suggested that its reaction with methyl dichloroacetate should yield methyl α,α-bis-(chloromethyl)-propionate. However, the product isolated appears to be methyl α,α-bis-(chloromethyl)-butyrate. Since initial free radical attack upon methyl dichloroacetate should yield the same free radical ($\cdot CCl_2COOCH_3$) as that obtained from methyl trichloroacetate, intermediate reaction steps (successive reactions with diazomethane and 1,2-shifts of chlorine) should be the same for the two esters. The observed result with methyl dichloroacetate may be attributed to its lesser reactivity in chain transfer with the free radical ($\cdot CH_2C(CH_2Cl)_2COOCH_3$). The latter apparently reacts with one more molecule of diazomethane ($\cdot CH_2C(CH_2Cl)_2COOCH_3 + CH_2N_2 \rightarrow \cdot CH_2CH_2C(CH_2Cl)_2COOCH_3 + N_2$) before transfer occurs.

Experimental Part

Reagents.—Eastman Kodak Co. carbon tetrabromide (m.p. 92.5°) was recrystallized from ethanol. Bromoform (b.p. 55–56° at 35 mm., $n^{20}D$ 1.5988, Mallinckrodt reagent grade) was washed with water, dried over anhydrous calcium chloride and distilled. Iodoform (m.p. 119°, Mallinckrodt reagent grade) was recrystallized from an ethanol-ethyl acetate mixture. The dibromodichloromethane used (b.p. 66° at 81 mm., $n^{20}D$ 1.5525) was obtained as a by-product in a previous preparation of bromotrichloromethane.[10] Methyl dichloroacetate (b.p. 62° at 40 mm., $n^{20}D$ 1.4420) was prepared from the acid and methanol in the presence of concentrated sulfuric acid. Eastman Kodak Co. chlorobenzene (b.p. 129–130°) was distilled through a 15-plate Fenske column.

Gaseous diazomethane (prepared by the addition of a slurry of N-nitroso-N-methylurea, 35 g., 0.34 mole, in methanol, 200 ml., to an aqueous potassium hydroxide solution, 70 ml., 40%) was swept as described previously[1] in a measured flow of nitrogen into the reaction vessel (same apparatus as in the previous study[1]) below the surface of the organic halide. The total sweep and evolved nitrogen was measured in a Precision Wet Test meter. The quantity of diazomethane generated (9.3 g., 0.225 mole, 66% yield) was determined as previously reported.[1]

The Reaction of Diazomethane with Carbon Tetrabromide.—In a typical experiment, diazomethane (9.3 g., 0.225 mole) was swept over a period of 1.5 hours by a stream of nitrogen (3.69 liters) into a solution of carbon tetrabromide (50 g., 0.15 mole) in chlorobenzene (110 g.) contained in the reaction tube illuminated internally by a mercury discharge tube. Within five minutes after its addition was complete, the yellow color of diazomethane disappeared from the solution and nitrogen evolution ceased. Total nitrogen measured by the Wet Test meter (10.5 liters) indicated its yield (6.8 l. at 25° and 750 mm., 0.27 mole) from the diazomethane generation and light reaction. Methyl ether (1.5 g.) was isolated from the cold trap used in the reaction apparatus, but not polymethylene separated from the reaction mixture.

The reaction mixture was distilled, and a series of fractions (b.p. 54–126°, total weight, 32.68 g., d^{30}_4 1.980–2.341) were obtained. Chlorobenzene (b.p. 129°, 107 g.) then distilled and a residue (17 g.) remained. The latter was recrystallized from ethanol and carbon tetrabromide (16 g., m.p. 88–90°) was recovered.

The preliminary fractions were shown to contain 1,1-dibromoethylene (recorded b.p. 90–91°, $d^{20.6}_4$ 2.178)[11] and dibromomethane (recorded b.p. 97°, d^{30}_4 2.471).[12] These fractions were combined and treated with excess bromine. The solution was then washed with sodium bisulfite solution and dried over anhydrous calcium chloride. Its distillation gave dibromomethane (9.4 g., 0.055 mole, b.p. 96–98°, d^{27}_4 2.400) and 1,1,1,2-tetrabromoethane (19.31 g., 0.055 mole, b.p. 103–104° at 15 mm., m.p. −17 to −15.8°, d^{25}_4 2.849[13]).

Anal. Calcd. for $C_2H_2Br_4$: Br, 92.5. Found: Br, 92.5.

A solution of the dibromomethane (0.5 g.) and sodium hydroxide (1.5 g.) in methanol (15 ml.) was held under reflux for one hour, and then distilled. The first fraction (5 ml.) with 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone of formaldehyde (m.p. 165°, mixed m.p. 165°). 1,1,1,2-Tetrabromoethane (14.1 g., b.p. 97–98° at 12 mm., d^{25}_4 2.849) prepared by the reaction of bromine with 1,1-dibromoethylene was identical in physical properties and infrared spectrum[14] with the above reaction product. The 1,1-dibromoethylene was prepared by the reaction of Eastman Kodak Co. 1,1,2-tribromoethane (15.1 g.) with sodium ethoxide in ethanol (1.35 g. of sodium with 13.5 ml. of absolute ethanol).[15]

In three separate reactions of diazomethane with carbon tetrabromide with the above conditions, the yields of 1,1-dibromoethylene (25%) were the same. These yields were determined as above by the conversion of this product to 1,1,1,2-tetrabromoethane (19.31–19.53 g.).

The Reaction of Diazomethane with Bromoform.—Diazomethane (9.3 g., 0.22 mole) was swept in a stream of nitrogen (6.0 l.) over a period of one hour into bromoform (264 g., 1.04 moles) illuminated internally by a mercury discharge tube. Nitrogen evolution ceased 1.5 hours after the addition was complete. The reaction mixture was then distilled and a series of fractions (b.p. 61.5–147°, 12.46 g., $d^{27.5}_4$ 2.296–2.734) were taken, and then bromoform (b.p. 59–60° at 40 mm., 245 g., $d^{27.5}_4$ 2.915) was recovered. A residue (4.2 g.) remained. None of these fractions gave a test (bromine in carbon tetrachloride) for the presence of unsaturates. The liquid condensed in the −80° trap attached to the distilling column was treated similarly with bromine and reaction to indicate a small amount of unsaturates occurred. Distillation of this reaction mixture gave methyl ether (4 g.) and a residue of brominated product too small for identification.

Initial fractions were combined and redistilled, and impure dibromomethane was obtained (b.p. 95–104°, 5.59 g., d^{28}_4 2.2951). The identity of this substance was confirmed as above by its hydrolysis and conversion of the product obtained to the 2,4-dinitrophenylhydrazone of formaldehyde (m.p. 159–160°). The identity of the latter substance was confirmed by "mixed melting point."

Molecular distillation of the reaction residue gave a viscous red oil (3.5 g.) and a black residue (0.7 g.). The distillate was analyzed.

Anal. Calcd. for $(CH_2CHBr)_x$: Br, 74.8. Found: Br, 81.45; mol. wt., 288.

The analysis suggests (approximate molecular formula, $C_4H_7Br_3$) that these products are telomers and polymers derived from vinyl bromide.

The Reaction of Diazomethane with Iodoform.—Diazomethane (9.3 g., 0.225 mole) was swept by a stream of nitrogen (3.7 l.) over a period of 2 hours into a solution of iodoform (120 g., 0.37 mole) in benzene (800 ml.) in a flask illuminated by a 150 watt Photoflood lamp. The expected amount of nitrogen (6.9 l.) was evolved, and the reaction ceased when the diazomethane addition was complete. No methyl ether or polymethylene was observed.

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(8) H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, **28**, 333 (1936).

(9) F. Asinger and F. Ebeneder, *Ber.*, **75**, 344 (1942).

(10) M. S. Kharasch, B. M. Kuderna and W. H. Urry, *J. Org. Chem.*, **13**, 895 (1948).

(11) R. Anschütz, *Ann.*, **221**, 140 (1883).

(12) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., New York, N. Y., 1950, p. 216.

(13) R. Anschütz, *Ann.*, **221**, 140 (1883).

(14) J. R. Eiszner, Ph.D. Dissertation, University of Chicago, 1952.

(15) T. Gray, *J. Chem. Soc.*, 1023 (1897).

The reaction mixture was distilled and the following fractions were obtained: 1, b.p. 55–56°, 4.3 g., 0.028 mole, iodoethylene[12]; 2, b.p. 56–79°, 10.5 g.; 3, b.p. 33.5° at 140 mm. 790 ml., recovered benzene; and 4, b.p. 59–66° at 11 mm., 28.9 g. The residue (74.2 g.) was recrystallized from methanol to give unreacted iodoform (59.6 g.). The remainder (14.6 g.) was insoluble in boiling methanol. To further confirm its identity as iodoethylene, a sample of fraction 1 (2 g.) in a solution containing mercuric acetate (4.33 g.), acetic acid (4 ml.) and water (0.33 ml.) was held at 100° for 5 hours in a bomb tube. Then the reaction mixture was distilled into a 2,4-dinitrophenylhydrazine solution. The 2,4-dinitrophenylhydrazone of acetaldehyde (m.p. 146–147°, m.p. of mixture with authentic sample 146–147°) was obtained. To determine further the yield of iodoethylene, fractions 2 and 3 were combined and treated with bromine until its color persisted. The reaction mixture was washed first with sodium bisulfite solution and then with water, and it was dried over anhydrous calcium chloride. Its distillation gave benzene and 1,2-dibromo-1-iodoethane (b.p. 92–94° at 14 mm., 11 g., 0.033 mole). This product was unstable and the distillate contained iodine. It was shaken with mercury, filtered and analyzed.

Anal. Calcd. for $C_2H_3Br_2I$: Ag equiv., 106.4. Found: Ag equiv., 107.7.

Fraction 4 was identified as diiodomethane. It was redistilled (b.p. 87–88° at 39 mm., 23.9 g., 0.09 mole, $d^{32.5}{}_4$ 3.312[16]), and a sample (4.2 g.) was heated with potasssium hydroxide (1 g.) in methanol (15 ml.) for one hour at 100° in a sealed tube. This reaction mixture was distilled, and the first distillate (5 ml.) was warmed with a solution of 2,4-dinitrophenylhydrazine in methanol containing sulfuric acid. The yellow crystals which formed (m.p. 162–163°) did not depress the melting point of an authentic sample of the 2,4-dinitrophenylhydrazone of formaldehyde.

The Reaction of Diazomethane with Dibromodichloromethane.—Diazomethane was prepared by the addition of N-nitroso-N-methylurea (35 g., 0.34 mole) in small portions to a mixture of chlorobenzene (320 g., 2.85 moles, redistilled b.p. 130.5°, $n^{20}D$ 1.5248) and potassium hydroxide solution (50%, 70 ml.) held at 0–5°. After the reaction was complete, the solution of diazomethane in chlorobenzene was separated and dried for 20 minutes at 0° over potassium hydroxide pellets. Iodometric titration[17] of an aliquot of it gave its diazomethane content (0.158 mole, 46% yield).

The solution of diazomethane (0.158 mole) in chlorobenzene and the dibromodichloromethane (514 g., 2.15 moles) were introduced dropwise simultaneously over a period of 15 minutes into a flask. Diffuse daylight and a 100 watt Mazda bulb four feet from the reaction flask were the only illumination, but reaction commenced immediately. As the reactants were mixed, nitrogen (3.0 l. at S.T.P., 85% yield) evolved and passed through the condenser and an attached −80° trap into a Precision West Test meter. The reaction mixture warmed from 25 to 45°. Strong illumination with a Photoflood lamp after the mixing gave no further nitrogen.

The reaction mixture was distilled through a 6-inch Fenske column, and a low boiling fraction (b.p. 31–128°, 10.12 g.) and a constant boiling mixture of unreacted dibromodichloromethane and chlorobenzene (b.p. 128°, 465 ml.) were obtained. A viscous liquid residue (11. g.) remained in the distilled flask. Redistillation of the low boiling fraction under nitrogen gave 1,1-dichloroethylene (b.p. 31–32°, 2.12 g., 0.022 mole, 12% yield) and dibromomethane (b.p. 95–100°, 5.73 g., 0.033 mole, 21% yield). In an earlier experiment, the 1,1-dichloroethylene was obtained in the same yield, but upon standing for 24 hours it was completely changed to a white polymeric solid. Its infrared spectrum was identical with that of 1,1-dichloroethylene (b.p. 31.7°, 60 g., 62% yield, $n^{20}D$ 1.4220, collected over β-naphthol) prepared by the reaction of 1,1,2-trichloroethane (Eastman Kodak Co., 124 g., 0.93 mole) with potassium hydroxide (56 g., 1.0 mole) in ethanol (450 ml.) held at 60° with stirring. The product was distilled (45–55°) through a small Vigreux column as the reaction progressed. The dibromomethane was further identified by heating a sample of it (1 g.) at 110° in a solution with sodium hydroxide (1 g.) and ethanol (95%, 7.5 ml.) for one hour in a bomb tube. Then additional ethanol (5 ml.) was added to the reaction mixture and it was distilled. From the first distillate fraction (5 ml.), bis-(2-hydroxynaphthyl)-methane (m.p. 180–182°—rapid heating, mixed m.p. with an authentic sample, 181–182°)[18] was prepared.

Study of the residue (11 g., average mol. wt. 489—in ebullioscope with carbon tetrachloride) indicated that it probably did not contain appreciable amounts of pentaerythrityl halides. Attempts to obtain crystals from it failed. Further, a solution of part of the residue (2 g., 0.004 mole) and sodium iodide (2 g., 0.134 mole) in acetone (10 ml.) was heated in a bomb tube at 120° for 66 hours. No solid material separated when the solution was cooled. The reaction mixture was then extracted with water (50 ml.). Iodine (0.0065 g., 0.0026 mole) in the aqueous extract was determined by titration with standard sodium thiosulfate solution. The semi-solid organic phase was dissolved in boiling methanol (200 ml.). Upon cooling, no separation of the very insoluble pentaerythrityl iodide[1] occurred. The formation of iodine in the reaction suggests that substances in the residue have halogen atoms on adjacent carbon atoms. However, probably components are products of addition of dibromodichloromethane to 1,1-dichloroethylene.

The Reaction of Diazomethane with Carbon Tetrabromide in the Presence of Diphenylamine.—A cold (10°) solution of diazomethane (6.6 g., 0.16 mole, prepared from N-nitroso-N-methylurea and analyzed as in the previous experiment) in chlorobenzene (350 ml.) and a solution of carbon tetrabromide (50 g., 0.15 mole) and diphenylamine (5 g., 0.03 mole) in chlorobenzene (100 ml.) were added dropwise simultaneously to a flask equipped with a magnetic stirrer. A gas exit tube attached to the top of the condenser was connected to a −80° trap and thence to a Precision Wet Test meter. No reaction was observed as these solutions were mixed with vigorous stirring. The temperature of the reaction mixture rose slowly to room temperature and then remained constant. No gas evolution was detected and the initial yellow color of the solution did not change.

After 25–30 minutes, the solution suddenly warmed to 40° and nitrogen (1.0 l.) was evolved during 10 minutes. Nitrogen (total 2.23 l., 64% of theory) evolution continued at a diminishing rate for 2 hours, and the reaction mixture became dark red in color. A gelatinous solid appeared in it. The −80° trap contained liquid diazomethane (0.11 g.) which was quantitatively determined by the volume of nitrogen obtained when acid was added to it.

The Quantum Yield of the Photochemical Reaction of Diazomethane with Carbon Tetrachloride.—This determination was made with an actinometric method (uranyl oxalate) in a special apparatus[19] in which a mercury resonance lamp was immersed in the reaction mixture held in a cylindrical reaction tube which was enclosed in a further tube to contain actinometer solution to permit measurement of light not absorbed in the reaction. The mercury lamp was a U-tube made of 8-mm. tubing with a quartz section (8 cm. in length) at the lower, semicircular end, and was filled according to the directions of Melville (90% of its total irradiation at 2537 Å.).[20] The lower part of the reaction tube (25 mm. in diameter) was a quartz section (7.5 cm. long) with its upper edge 2 cm. above the top of the quartz part of the discharge tube. A condenser was attached to the reaction tube, and another one was connected to the outer tube. Solutions in both tubes were stirred by curved, magnetically-driven stirring bars, and temperature was measured by an Anschütz thermometer mounted in the reaction tube.

A constant wattage (120 watts) for the discharge tube was arranged by the passage of line current (115 volts a.c.) through a variable transformer with its secondary circuit set at 83 volts to a Sola constant voltage transformer which delivered at a constant 115 volts, and the latter was connected to a high voltage transformer (secondary at 6000 volts). Leads from the secondary circuit of the latter were connected to the electrodes (steel encased in mica) of the discharge tube. With the described circuit, current through the lamp as measured by a microammeter in series was constant at 20 ma.

The quantum output of the discharge tube (4.5×10^{16} quanta sec.$^{-1}$) was determined at 0–2° with the both tubes of the apparatus filled to a level 4 cm. above the quartz sec-

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[20] H. W. Melville, *Trans. Faraday Soc.*, **32**, 1525 (1936).

tions with actinometer solution[21] (with optimum concentrations to give a quantum yield of 0.60 at 2537 Å.—about 0.01 *M* in uranyl sulfate and 0.025 *M* in oxalic acid). Titration of an aliquot portion (10 ml.) of this solution required 41.6 ml. of 0.0114 *N* potassium permanganate solution (0.0474 *N* oxalic acid). The stirred actinometer solution (80 ml. in the reaction tube) was irradiated for 2400 seconds (0–2°, with the apparatus immersed in an ice–water-bath) after which an aliquot portion (10 ml.) required 39.2 ml. of the permanganate solution (0.11 millimole of oxalic acid consumed in the 80-ml. solution). The remaining solution (70 ml.) was then irradiated for an additional 1800 seconds and titration of a 10-ml. aliquot required 37.2 ml. of the permanganate solution (0.080 millimole of oxalic acid used in the 70-ml. solution).

The reaction tube was then filled to the same level with a solution of diazomethane (from N-nitroso-N-methylurea, 18 g., 0.174 mole) in carbon tetrachloride (100 ml., $n^{20}\text{D}$ 1.4600). The outer tube was filled with actinometer solution, and the apparatus was immersed in an ice–water-bath which held the reaction temperature at 0–2°. Irradiation of the reaction mixture for two successive periods (300 seconds each) gave nitrogen (149 ml. at S.T.P.) from reaction of diazomethane (6.65 millimoles) in each time period. The calculated gross quantum yield was 298. During the reaction experiment and the quantum output determination the light was completely absorbed by the contents of the reaction tube. The oxalic acid concentration of the actinometer solution in the outer tube did not change.

The Reaction of Diazomethane with Methyl Dichloroacetate.—In a stream of nitrogen (5.2 l.), diazomethane (17.3 g., 0.41 mole) was swept over a period of two hours into methyl dichloroacetate (166 g., 1.19 moles) illuminated internally with the mercury discharge tube. Two additional hours of illumination were needed before nitrogen evolution ceased. Total nitrogen volume measured by the Precision Wet Test meter (15.7 l.) indicated its yield (10.5 l. at 25° and 750 mm., 0.42 mole, 100% yield) from the diazomethane generation and light reactions. Methyl ether (2.5 g.) and polymethylene (0.04 g.) were obtained.

The reaction mixture was distilled to give recovered methyl dichloroacetate (b.p. 45.5–46° at 14 mm., 152 g.) and a product fraction (b.p. 46–67° at 14 mm., 16.94 g.). A residue (1.8 g.) remained in the distilling flask. The product was redistilled to give the following fractions: 1, b.p. 47–49° at 14 mm., 1.83 g.; 2, b.p. 49–64° at 14 mm., 3.22 g.; 3, b.p. 54–59.5° at 14 mm., 2.88 g., and 4, b.p. 59.5–68° at 14 mm., 2.27 g. Analysis of these fractions indicated that they contain little of the expected methyl α,α-bis-(chloromethyl)-propionate ($C_6H_{10}O_2Cl_2$, fraction 1 is apparently in part unreacted methyl dichloroacetate), and that the dominant product is probably methyl α,α-bis-(chloromethyl)-butyrate ($C_7H_{12}O_2Cl_2$).

Anal. Calcd. for $C_6H_{10}O_2Cl_2$: Cl, 38.3; mol. wt., 185; for $C_7H_{12}O_2Cl_2$: Cl, 35.6; mol. wt., 199. Found: fraction 1, Cl, 42.0; mol. wt., 185; fraction 2, Cl, 35.8; mol. wt., 190; fraction 3, Cl, 35.6; mol. wt., 198; fraction 4, mol. wt., 203.

Fractions 2 and 3 were combined and reduced with excess lithium aluminum hydride (0.1 *N* solution in ether). The resulting alcohol gave an α-naphthylurethan (m.p. 159.5–160°) which gave the correct analysis for that of 2,2-bis-(chloromethyl)-butanol-1.

Anal. Calcd. for $C_{17}H_{19}O_2NCl_2$: C, 60.01; H, 5.63; Cl, 20.84. Found: C, 59.49; H, 5.61; Cl, 20.92.

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[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Ethylenimine Ketones. XI.[1] Steric Controls in the Formation of Isomeric Ethylenimine Ketones

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A study of the reaction of α-bromo-α,β-unsaturated ketones with primary amines indicates that the ethylenimine ketone *cis/trans* product ratio which results is nearly the same as that observed for the analogous reactions with the corresponding α,β-dibromoketones. Evidence is presented to support a rationale to explain the ethylenimine ketone *cis/trans* product ratio based on relative group sizes in the intermediate α-bromo-β-aminoketones and favored conformations in transition states. The reaction of N-bromocyclohexylamine and cyclohexylamine with *p*-phenylcrotonophenone by various procedures produced the *cis*-ethylenimine ketone which is the major, though not exclusive, product from the reaction of α-bromo-*p*-phenylcrotonophenone and cyclohexylamine, indicating that similar steric controls operate in these diverse reactions. Several new examples of the N-iodo amine reaction with α,β-unsaturated ketones to produce only *trans*-ethylenimine ketones have been performed. An explanation of the relative adsorptivity of *cis*- and *trans*-ethylenimine ketones on activated alumina is presented.

A comparison of the ratios of the amounts of the *cis* and *trans* isomeric forms of ethylenimine ketones resulting from the reactions of primary amines with 4′-phenylchalcone dibromide[2] and *p*-phenylcrotonophenone dibromide[1] suggests that steric controls are operating during the formation of the products. With the former dibromide,[2] cyclohexylamine produced 47% of the *cis* isomer and 44% of the *trans* isomer[2] of 1-cyclohexyl-2-phenyl-3-(*p*-phenylbenzoyl)-ethylenimine, while methylamine gave 20% of the *cis* and 70% of the *trans* isomer[2] of 1-methyl-2-phenyl-3-(*p*-phenylbenzoyl)-ethylenimine with the same dibromide.[2] With the latter dibromide,[1] cyclohexylamine formed 59% of the *cis*- and 33% of the *trans*-1-cyclohexyl-2-methyl-3-(*p*-phenylbenzoyl)-ethylenimine.[1]

It has been postulated that the first step in the reaction of a primary amine with an α,β-dibromoketone is the formation of the α-bromo-α,β-unsaturated ketone. This is then followed by a 1,4-addition of the amine to produce the α-bromo-β-aminoketones.[3] It has been pointed out[2] that these intermediate α-bromo-β-aminoketones must exist as varying mixtures of the diastereoisomeric *erythro* and *threo* forms. An internal SN2 type ring closure would then be expected to produce the mixed *cis*- and *trans*-ethylenimine ketones. A study of the mechanism and stereochemistry of three-ring cleavage and closure[4] has revealed the fact that each ring closure of the halo amino ketones involves a Walden inversion. This suggests that the ethylenimine ketone *cis/trans* ratio is determined by the product ratio of the intermediate

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[1] For paper X, see N. H. Cromwell and R. J. Mohrbacher, THIS JOURNAL, **75**, 6252 (1953).

[2] N. H. Cromwell and M. A. Graff, *J. Org. Chem.*, **17**, 414 (1952).

[3] N. H. Cromwell and D. J. Cram, THIS JOURNAL, **65**, 301 (1943).

[4] N. H. Cromwell, *et al.*, *ibid.*, **75**, 5384 (1953).