Oxidation of 1,1-Dimesitylpropene.—To a solution of 13.6 g. of 1,1-dimesitylpropene in 500 ml. of glacial acetic acid was added 16.5 g. of chromium trioxide. The mixture warmed spontaneously and was cooled in an ice-bath to 35°. After the mixture had been allowed to stand overnight, it was diluted with 2 l. of water. The resulting suspension stood for 24 hours, during which time most of the oxidation product precipitated as a sticky solid. The water–acetic acid mixture was extracted with three 300-ml. portions of ether; the ether solution was washed with 10% sodium hydroxide and then with a 10% sodium carbonate solution until no more carbon dioxide was evolved, and finally was dried over sodium carbonate. After the ether was removed the residue (about 8 g.) partially crystallized when it was allowed to stand overnight in the refrigerator. It was triturated with 10 ml. of absolute ethanol and filtered. The yield of light brown crystals of m.p. 138–141° was 2.0 g. After repeated crystallization, the crystals melted at 144–146° and did not depress the melting point of a known sample of α,α-dimesitylacetone. Infrared analysis also showed the two to be identical.

Oxidation of 1,1-Dimesitylbutene.—The oxidation was carried out with 14.2 g. of 1,1-dimesitylbutene and 16.5 g. of chromium trioxide, and the product extracted as described above. Evaporation of the ether left 10 to 15 ml. of a yellow oil which partially crystallized overnight. After three recrystallizations from ethanol, the product melted at 133–135.5°. This oxidation product probably is 1,1-dimesityl-1-butene-3-one.

Anal. Calcd. for $C_{22}H_{26}O$: C, 86.23; H, 8.55. Found: C, 86.07; H, 8.51.

The infrared spectrum of this substance indicates the presence of a conjugated carbonyl group; a positive test with the dinitrophenylhydrazine reagent was observed.

URBANA, ILLINOIS

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

Photochemical Reactions of Diazomethane with Polyhalomethanes and α-Haloesters[1]

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

RECEIVED JUNE 16, 1952

The novel light-induced reaction of diazomethane with carbon tetrachloride gives 1,3-dichloro-2,2-bis-(chloromethyl)-propane and nitrogen. Analogous reactions with bromotrichloromethane and chloroform yield 1,3-dichloro-2-bromomethyl-2-chloromethylpropane and 1,3-dichloro-2-chloromethyl-2-methylpropane, respectively. α-Haloesters undergo similar reactions: methyl trichloroacetate to give methyl tris-(chloromethyl)-acetate, and ethyl bromoacetate and methyl α-bromopropionate to give ethyl β-bromopropionate and methyl β-bromoisobutyrate, respectively. A free-radical, chain mechanism is proposed since these reactions exhibit the following characteristics: (1) light initiation, (2) inhibition by antioxidants and (3) zero order kinetics at constant temperature and light intensity.

In the light-induced reactions of diazomethane with polyhalomethanes to yield polyhaloneopentane derivatives and with α-haloesters to give β-haloesters, a methylene group is interposed between each halogen atom in the organic halide and the carbon atom to which it is attached ($CCl_4 \rightarrow C(CH_2Cl)_4$; $Cl_3CCOOCH_3 \rightarrow (ClCH_2)_3COOCH_3$). This paper records the results of an investigation of the scope and mechanism in this reaction.

In this study, solutions of diazomethane in many organic halides have been irradiated, but this reaction has been observed only with some of those which undergo the free radical chain reaction addition to olefins.[2-4] The following reactions have been effected (yields in parentheses).

$$CCl_4 + 4CH_2N_2 \longrightarrow C(CH_2Cl)_4\ (60\%) \quad (1)$$

$$BrCCl_3 + 4CH_2N_2 \longrightarrow BrCH_2C(CH_2Cl)_3\ (40\%) \quad (2)$$

$$HCCl_3 + 4CH_2N_2 \longrightarrow CH_3C(CH_2Cl)_3\ (45\%) \quad (3)$$

$$Cl_3CCOOCH_3 + 3CH_2N_2 \longrightarrow (ClCH_2)_3CCOOCH_3\ (60\%) \quad (4)$$

$$CH_3CHBrCOOCH_3 + CH_2N_2 \longrightarrow CH_3CH(CH_2Br)COOCH_3\ (20\%) \quad (5)$$

$$BrCH_2COOCH_3 + CH_2N_2 \longrightarrow BrCH_2CH_2COOCH_3 \quad (6)$$

In each of these reactions the expected amount of nitrogen was evolved, and two products of side reactions were obtained in small amount: polymethylene and the methyl ether (methyl ether and methyl ether ether) derived from the alcohol used as solvent in the preparation of the diazomethane.

The required analytical results and the following evidence for the assigned structures of the products in these reactions (1 to 6) were obtained: (1) The 1,3-dichloro-2,2-bis-(chloromethyl)-propane was identical with a synthetic sample prepared by the reaction of thionyl chloride with pentaerythritol in pyridine.[5] (2) The structure of the 1,3-dichloro-2-bromomethyl-2-chloromethylpropane was confirmed by its identity with an authentic sample prepared by the reaction of 1,3-dichloro-2-chloromethyl-2-hydroxymethylpropane (prepared by the method of Mooradian and Cloke[5]) with phosphorus tribromide. It was converted to 1,3-diiodo-2,2-bis-(iodomethyl)-propane by reaction with sodium iodide in acetone (72 hr. in a bomb tube at 120°). (3) The 1,3-dichloro-2-chloromethyl-2-methylpropane was shown to be identical in index of refraction, specific gravity, boiling point and infrared spectrum (Fig. 1) with the substance prepared by the reaction of 2-hydroxymethyl-2-methyl-1,3-propanediol (prepared by the base-catalyzed reaction of propionaldehyde with formaldehyde) with thionyl chloride in pyridine. (4) The structure of methyl tris-(chloromethyl)-acetate was identified by its two step conversion (reactions 7 and 8) to 1,3-dichloro-2,2-bis-(chloromethyl)-propane. (5) The refractive index and boiling point of the methyl β-

$$(ClCH_2)_3CCOOCH_3 \xrightarrow{LiAlH_4} (ClCH_2)_3CCH_2OH \quad (7)$$

$$(ClCH_2)_3CCH_2OH + SOCl_2 \xrightarrow{pyridine} C(CH_2Cl)_4 \quad (8)$$

---

[1] Previous communications; W. H. Urry and J. R. Eiszner, THIS JOURNAL, **73**, 2977 (1951). A part of this work was presented in summary at the Twelfth Annual Organic Symposium in Denver, Colorado, June, 1951.

(2) M. S. Kharasch, W. H. Urry and E. V. Jensen, THIS JOURNAL, **67**, 1626 (1945).

(3) M. S. Kharasch, E. V. Jensen and W. H. Urry, *ibid.*, **69**, 1100 (1947).

(4) M. S. Kharasch, O. Reinmuth and W. H. Urry, *ibid.*, **69**, 1105 (1947).

(5) A. Mooradian and J. B. Cloke, *ibid.*, **67**, 942 (1945).

bromoisobutyrate were the same as those recorded by Price and Coyner.[6] The ester was hydrolyzed to give β-bromoisobutyric acid. (6) The reaction product of diazomethane with methyl bromoacetate could not be separated from the unchanged ester by distillation through the all-glass fractionating columns appropriate for halide separations. The mixture was hydrolyzed with concentrated hydrobromic acid, and the bromoacetic and β-bromopropionic acids were separated by chromatography on a silicic acid column. The β-bromopropionic acid obtained was shown to be the same as a synthetic sample.

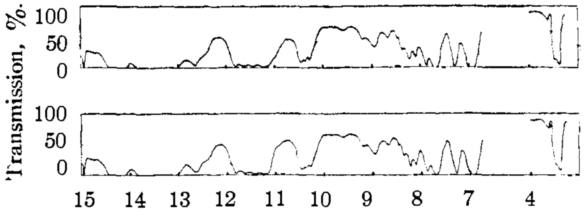

Fig. 1.—Infrared absorption spectra (Perkin–Elmer infrared spectrophotometer, model 12 C) of 1,3-dichloro-2-chloromethyl-2-methylpropane from the diazomethane–chloroform reaction (upper), and from the reaction of 2-hydroxymethyl-2-methylpropanediol-1,3 with thionyl chloride (lower).

The methyl ether formed in small yield when methyl alcohol was used as the solvent in the diazomethane preparation was identified by its vapor pressure at −80°, its molecular weight, and its reaction with concentrated hydriodic acid to give methyl iodide which gave N-methylpyridinium iodide with pyridine. The methyl ethyl ether obtained when ethyl alcohol was used as the solvent was identified by its molecular weight and its vapor pressure at −80°.

Discussion

A free radical, chain mechanism for these reactions of diazomethane is suggested by the following experimental observations: (1) equal volumes of nitrogen are evolved per unit times at constant light intensity and temperature (during the first 70% of reaction), and hence the reaction is of zero order, (2) it is light-induced (see Fig. 2), (3) it is inhibited by diphenylamine (see Experimental part), and (4) it is observed only with organic halides known to undergo the free radical, chain reaction addition to olefins. Further facts, however, make it unlikely that a sequence of reactions involving stable molecules [$CCl_4 \rightarrow Cl_3CCH_2Cl$ (I) $\rightarrow Cl_2C(CH_2Cl)_2$ (II) $\rightarrow ClC(CH_2Cl)_3$ (III) $\rightarrow C(CH_2Cl)_4$] occurs. The reaction could proceed in this manner only if intermediate substances (I, II and III) were far more reactive with diazomethane than carbon tetrachloride (present in great excess), but 1,1,1,2-tetrachloroethane (I) does not give this reaction with diazomethane. Also, 1,1,1-trichloroethane (the possible first intermediate in the reaction with chloroform) failed to give this reaction. Also, the substances I, II and III were not found in the reaction products, and if they are formed they are present in quantities too small for isolation.

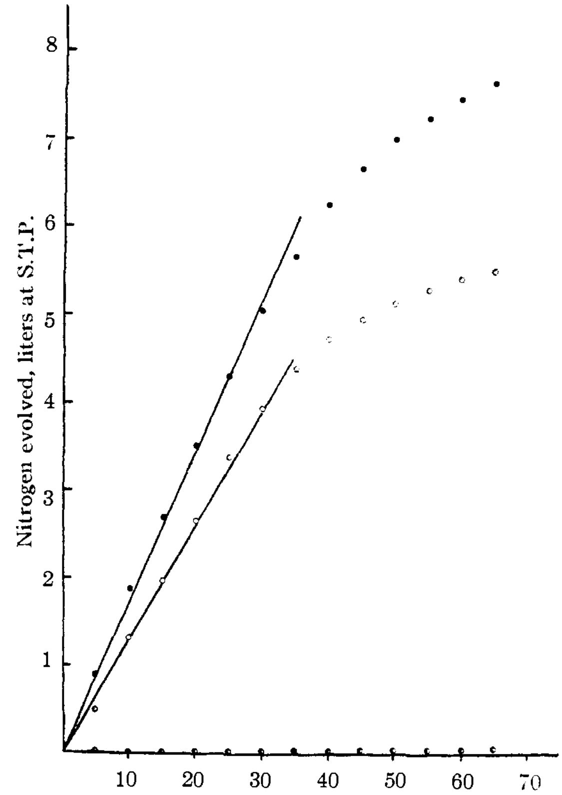

Fig. 2.—Rate of nitrogen evolution in the reactions of diazomethane with ethyl bromoacetate, ●, with carbon tetrachloride, O, in the light; and with carbon tetrachloride, ◐, in the dark.

The accumulated evidence favors, therefore, a free radical, chain reaction mechanism involving only unstable intermediates. The sequence proposed below for the reaction of diazomethane with carbon tetrachloride fulfills this condition by the postulation of successive free radical rearrangements (1,2-shifts of chlorine) alternating with reactions with diazomethane. Such free radical rearrangements (involving phenyl migration) have been observed in the reactions of the free neophyl (β-methyl-β-phenylpropyl) radical.[7,8] Reactions 1 and

$$CH_2N_2 \xrightarrow{h\nu} :CH_2 + N_2 \qquad (1)$$
$$:CH_2 + CCl_4 \longrightarrow \cdot CH_2Cl + Cl_3C\cdot \qquad (2)$$
$$Cl_3C\cdot + CH_2N_2 \longrightarrow Cl_3CCH_2\cdot + N_2 \qquad (3)$$
$$Cl_3CCH_2\cdot \longrightarrow Cl_2\underset{\cdot}{C}CH_2Cl \qquad (4)$$
$$Cl_2\underset{\cdot}{C}CH_2Cl + CH_2N_2 \longrightarrow Cl_2C(CH_2Cl)CH_2\cdot \qquad (5)$$
$$Cl_2C(CH_2Cl)CH_2\cdot \longrightarrow Cl\underset{\cdot}{C}(CH_2Cl)_2 \qquad (6)$$
$$Cl\underset{\cdot}{C}(CH_2Cl)_2 + CH_2N_2 \longrightarrow ClC(CH_2Cl)_2CH_2\cdot \qquad (7)$$
$$ClC(CH_2Cl)_2CH_2\cdot \longrightarrow \cdot C(CH_2Cl)_3 \qquad (8)$$
$$\cdot C(CH_2Cl)_3 + CH_2N_2 \longrightarrow \underset{\cdot}{C}H_2C(CH_2Cl)_3 \qquad (9)$$
$$\cdot CH_2C(CH_2Cl)_3 + CCl_4 \longrightarrow C(CH_2Cl)_4 + Cl_3C\cdot \qquad (10)$$

2 are the chain-initiating, and reactions 3 to 10 are the chain-propagating steps. No evidence is at present available regarding chain termination.

---

[6] C. C. Price and E. C. Coyner, THIS JOURNAL, **62**, 1306 (1940).

[7] W. H. Urry and M. S. Kharasch, *ibid.*, **66**, 1438 (1944).

[8] S. Winstein and F. H. Seubold, *ibid.*, **69**, 2916 (1947).

This reaction scheme must be modified with the other halides studied. In the reactions with chloroform and bromotrichloromethane, the chain-initiating step (reaction 2) apparently involves the removal of a hydrogen atom or a bromine atom, respectively. Subsequent reactions (3, 4, 5, 6, 7, 8 and 9) are the same as given, but again in reaction 10 a hydrogen atom is removed from chloroform and a bromine atom from bromotrichloromethane. The reaction sequence is less complicated with the α-haloesters studied. With methyl trichloroacetate, it is proposed that (1) a chlorine atom is removed as in reaction 2, (2) five reaction steps then occur involving reactions of intermediate free radicals with diazomethane alternating with 1,2-shifts of chlorine atoms, and (3) the resulting free radical $[(ClCH_2)_2\underset{\cdot}{C}H_2COOCH_3]$ attacks methyl trichloroacetate to give the reaction product, $(ClCH_2)_3CCOOCH_3$, and another free radical $(Cl_2\underset{\cdot}{C}COOCH_3)$ to continue the chain sequence. The reaction with α-bromoesters apparently involves no rearrangement.

$$:CH_2 + BrCH_2COOCH_3 \longrightarrow \cdot CH_2Br + \cdot CH_2COOCH_3 \quad (11)$$

$$\cdot CH_2COOCH_3 + CH_2N_2 \longrightarrow \cdot CH_2CH_2COOCH_3 + N_2 \quad (12)$$

$$\cdot CH_2CH_2COOCH_3 + BrCH_2COOCH_3 \longrightarrow BrCH_2CH_2COOCH_3 + \cdot CH_2COOCH_3 \quad (13)$$

The proposal that the free radical, chain reaction is initiated by the photochemical dissociation of diazomethane (reactions 1 and 2) rather than that of the organic halide is supported by the following observations: (1) diazomethane absorbs light at longer wave lengths (predissociation bands beginning at 4700 Å., and a continuum at 4200 Å.),[9] and it has been shown to undergo photochemical dissociation in the vapor phase to give methylene[10]; (2) the slow dark reaction observed (Fig. 2) is probably due to the decomposition of the diazomethane either upon the rough glass surfaces of the reaction vessel or with catalytic impurities; and (3) the light-induced reactions of diazomethane with α-bromoesters must be initiated in this way (diazomethane + $h\nu$) since it has been shown that these esters will not undergo a light-initiated addition to olefins and hence probably do not undergo photochemical dissociation with visible light.[11]

Possible competing reactions of intermediate free radicals with either the diazoalkane or the organic halide impose stringent requirements if the observed self-sustaining chain reaction is to occur. The organic halide must be reactive enough to undergo reaction 2 and 10 with ease, but it must not be so reactive that it reacts prematurely with the free radicals in reactions 3 to 9. The diazo compound must be of such a nature that (1) the methylene produced in its photochemical dissociation is reactive enough to remove an atom from the organic halide (diphenyldiazomethane failed in this respect: its light reaction in bromotrichloromethane gave benzophenone azine), and (2) the free radicals formed as in reactions 3, 5, 7 and 9 will rearrange (in the cases studied the reactions such as 4, 6 and 8 constitute rearrangements to more stable free radicals). The reactions of methyl chloroacetate and methyl dichloroacetate with diazomethane to give products having a wide range of boiling points may be attributed to the failure of these halides to react readily as in reaction 10. The intermediate free radicals continue to add to diazomethane in varying proportions before a stable product results by reaction with an α-chloroester molecule to give a variety of homologous products. In the reactions of carbon tetrabromide and bromoform, the formation of low boiling and polymeric bromides suggests that the intermediate free radicals react to lose a bromine atom ($Br_3CCH_2\cdot \rightarrow Br\cdot + Br_2C{=}CH_2$). These reactions require further investigation. The reactions of benzyl bromide, benzotrichloride, 1,1,1,3-tetrachloropropane and *t*-butyl chloride under these conditions with diazomethane gave only small yields of high boiling products.

The occurrence of these free radical, chain reactions with diazomethane suggests that other reactions of aliphatic diazo compounds may proceed by a similar mechanism. The reaction of hexaphenylethane with diazomethane in ether solution to give 1,1,1,3,3,3-hexaphenylpropane probably proceeds as[12]

$$(C_6H_5)_3C\cdot + CH_2N_2 \longrightarrow (C_6H_5)_3CCH_2\cdot + N_2 \quad (14)$$

$$(C_6H_5)_3CH_2\cdot + (C_6H_5)_3CC(C_6H_5)_3 \longrightarrow (C_6H_5)_3CCH_2C(C_6H_5)_3 + (C_6H_5)_3C\cdot \quad (15)$$

A similar reaction scheme seems likely for the observed reactions of aliphatic diazo compounds with disulfides and sulfenyl chlorides.[13,14] The light-induced reactions of diazomethane with ethyl ether, tetrahydrofuran and isopropyl alcohol to give homologous products[15] probably even more closely resemble the reactions reported here.

Experimental Part

Reagents.—Mallinckrodt reagent grade carbon tetrachloride (b.p. 74.6°, $n^{20}D$ 1.4558) was distilled before use. Chloroform (b.p. 61°, $n^{20}D$ 1.4450, Mallinckrodt reagent grade) was washed with water, dried over anhydrous calcium chloride and distilled. The methyl trichloroacetate (b.p. 149–150°, $n^{20}D$ 1.4571), methyl α-bromopropionate (b.p. 51–51.5° at 10 mm., $n^{20}D$ 1.4463) and ethyl bromoacetate (b.p. 51.2° at 15 mm., $n^{20}D$ 1.4519) were prepared from the corresponding acids by their reactions with the alcohols in the presence of concentrated sulfuric acid. They were washed with dilute sodium bicarbonate solution, dried over anhydrous sodium sulfate, and distilled.

Gaseous diazomethane was prepared by the addition of a slurry of N-nitroso-N-methylurea (35 g., 0.34 mole) in methanol or ethanol (200 ml.) to a magnetically stirred aqueous potassium hydroxide solution (70 ml., 40%). After the slurry addition was complete, water (100 ml.) was added. The liberated diazomethane was swept by a measured flow of nitrogen into the reaction vessel (either a cylindrical tube illuminated internally by a mercury discharge tube coil or a 2-liter flask illuminated from without by a 150-watt spotlight) and was introduced below the surface of the organic halide. The reaction vessel was equipped with a condenser cooled to −80°. Evolved and sweep gases

---

[9] R. G. W. Norrish and F. W. Kirkbride, *J. Chem. Soc.*, 119 (1933).

[10] T. G. Pearson, R. H. Purcell and G. S. Saigh, *ibid.*, 409 (1938).

[11] M. S. Kharasch, P. S. Skell and P. Fischer, THIS JOURNAL, **70**, 1055 (1948).

[12] W. Schlenk and C. Bornhardt, *Ann.*, **394**, 183 (1912).

[13] A. Schönberg and his co-workers, *Ber.*, **62**, 440 (1929); **63**, 3102 (1930); **66**, 1932 (1933).

[14] R. Stolle, F. Henke-Stark and H. Perrey, *ibid.*, **62**, 1112 (1929).

[15] H. Meerwein, H. Rathjen and H. Werner, *ibid.*, **75**, 1610 (1942).

passed through it to a trap held at −80° and then through a Precision Wet Test Meter. Usually about 6 liters of sweep nitrogen was used, and the total nitrogen evolved from the reactions occurring both in the diazomethane generation reaction and in the reaction with the organic halide was from 7.15 to 7.70 liters (0.33 to 0.34 mole). The amount of nitrogen derived from side reactions in the diazomethane generation was from 1.95 to 2.88 liters (0.087 to 0.13 mole; see Reaction Rate Studies).

To calculate reaction yields it was important to know the amount of diazomethane which reached the illumination vessel. The product from a reaction as described above was swept into an ether solution containing a known amount of benzoic acid. Titration following the reaction showed that 9.3 g. (0.225 mole, 66% yield, used as the basis of yield calculations) of diazomethane was obtained. The above reagents in a two-phase reaction mixture with ether give diazomethane[16] (10.5–12.6 g., 0.25–0.30 mole) in greater yield (74–88%) because (1) the temperature is lower (our reaction mixtures were allowed to reach temperatures of about 50°) and (2) the ether dissolves the diazomethane and reduces its contact with the strong base.

The Reaction of Diazomethane with Carbon Tetrachloride.—In a typical experiment, diazomethane (9.3 g., 0.225 mole) was swept in a stream of nitrogen (total 6 liters) over a period of 2 hours into carbon tetrachloride (185 g., 1.2 moles) illuminated in the reaction vessel equipped with the internal mercury discharge lamp. The yellow color of the diazomethane disappeared and nitrogen evolution ceased after an additional hour. The total nitrogen obtained from the light and diazomethane generation reactions was 7.55 liters (total 13.55 liters at S.T.P. measured on the meter).

The reaction mixture was filtered to remove precipitated polymethylene (0.025 g.) and was distilled through a 12-plate fractionating column packed with single-turn glass helices. After unreacted carbon tetrachloride (b.p. 74.6°, n^{20}D 1.4558) had distilled, a residue (7.2 g.), which solidified upon cooling, remained. The solid was sublimed (10 mm.) and pure 1,3-dichloro-2,2-bis-(chloromethyl)-propane (3.89 g., m.p. 96.3–97°, yield based upon crude product 60%) was obtained. The m.p. of a mixture with an authentic sample[5] showed no depression.

Anal. Calcd. for $C_5H_8Cl_4$: C, 28.59; H, 3.85; Cl, 67.56; mol. wt., 210. Found: C, 28.59; H, 4.03; Cl, 67.39; mol. wt. (benzene f.p. lowering), 208.

A residue (0.5 g.) remained in the sublimation vessel.

The −80° trap attached to the distilling column contained a liquid which was shown to be methyl ether (3.0 g., 0.065 mole, 28% yield). It was transferred to the vacuum line, and its molecular weight (46.6, gas density balance, calcd. for C_2H_6O, 46) and its vapor pressure (36 mm. at −80°) were measured. The methyl ether (3.0 g.) was treated in a bomb tube with concentrated hydriodic acid (45 ml.) at 100° for 5 hours. Methyl iodide (8.1 g.) separated, and a portion of it (0.4 g.) was treated with pyridine (0.05 g.) to give N-methylpyridinium iodide (m.p. 116–117°; m.p. of mixture with authentic sample, 116–117°). This low boiling reaction product did not contain methyl chloride. No precipitate formed when it was heated with alcoholic silver nitrate at 100° for 48 hours.

When ethanol was used as the solvent in the preparation of the diazomethane, methyl ethyl ether was obtained in about the same quantity. It was identified by its vapor pressure (4 mm. at −80°) and its molecular weight (59.7, gas density balance, calcd. for C_3H_8O, 60).

The reaction with carbon tetrachloride was performed seven times. It was more rapid in the spotlight apparatus than in the mercury coil reaction vessel. The yields of crude 1,3-dichloro-2,2-bis-(chloromethyl)-propane (6.2–7.2 g.) and dimethyl ether (3.0–5.6 g.) differed little. Differences were probably due to variable losses of the products due to their volatility.

The Reaction of Diazomethane with Bromotrichloromethane.—A solution of diazomethane (10.5 g., 0.25 mole) in ether (500 ml.) was added to bromotrichloromethane (457 g., 2.25 moles). The reaction mixture was illuminated only by room light (daylight tubes), and the reaction was complete after 2 hours. The ether and unreacted bromotrichloromethane (b.p. 103.5°, n^{20}D 1.5071) were distilled. The dark semisolid residue (6.3 g.) was treated with Norite and recrystallized from ethyl alcohol to give white crystals of 1,3-dichloro-2-bromomethyl-2-chloromethylpropane (3.4 g., 0.014 mole; 38% yield, m.p. 103.7–104°, m.p. of the mixture with an authentic sample 104°).

Anal. Calcd. for $C_5H_8Cl_3Br$: C, 23.64; H, 3.17; Ag equiv., 63.6; mol. wt., 254. Found: C, 23.67; H, 3.47; Ag equiv., 65.8; mol. wt. (benzene f.p. lowering), 257.

The lower yield in this reaction is attributed to side reactions of diazomethane with the ether.

The synthetic sample of 1,3-dichloro-2-bromomethyl-2-chloromethylpropane (m.p. 104°) was prepared by the reaction of 1,3-dichloro-2-hydroxymethyl-2-chloromethylpropane (prepared[5] from pentaerythritol, 21.4 g., thionyl chloride, 56 g., and pyridine, 37.3 g.) with phosphorus tribromide at 170° for six hours. The structure was confirmed by conversion of the diazomethane–bromotrichloromethane product (0.4 g.) to 1,3-diiodo-2,2-bis-(iodomethyl)-propane (0.5 g., m.p. 233°) by its reaction with sodium iodide (2.0 g.) and acetone (10 ml.) in a bomb tube at 120° for 72 hours. The m.p. of a mixture with an authentic sample (prepared with the same conditions from 1,3-dichloro-2,2-bis-(chloromethyl)-propane) gave no depression.

The Reaction of Diazomethane with Chloroform.—In a typical experiment, diazomethane (9.3 g., 0.225 mole) was swept (with 6 l. of nitrogen) into chloroform (258 g., 2.16 mole) in the mercury coil reaction vessel. Nitrogen (2.4 l.) was evolved in the diazomethane generation. The mercury discharge tube was turned on and the reaction was complete after 2 hours (5.2 liters of nitrogen obtained). The unreacted chloroform (b.p. 59–60°, n^{20}D 1.4448) was recovered by distillation through the 50-plate column. The distillation residue (5.0 g.) was distilled through a small Vigreux column to give 1,3-dichloro-2-chloromethyl-2-methylpropane (3.9 g., n^{20}D 1.4837, d^{20}_4 1.264, b.p. 64–65° at 8 mm., 45% yield).

Anal. Calcd. for $C_5H_9Cl_3$: C, 34.23; H, 5.17; Cl, 60.61. Found: C, 34.47; H, 5.40; Cl, 59.61.

A residue (0.5 g.) remained in the distilling flask.

1,3-Dichloro-2-chloromethyl-2-methylpropane prepared as follows was shown to be identical with the above product (infrared analysis, Fig. 1). Thionyl chloride (35 g., 0.30 mole) was added to a solution containing 2-hydroxymethyl-2-methylpropanediol-1,3 (9.7 g., 0.082 mole, m.p. 189–191°, prepared by the method of Hosaeus[17] from formaldehyde, 80 g. of 40% solution in water, propionaldehyde, 20 g., and calcium oxide, 50 g.) and pyridine (4 g.) held at 0°. The reaction mixture was heated under reflux for 2 hours, and then poured into water (25 ml.). The oily product was taken up in ether and dried over anhydrous calcium chloride. Distillation gave 1,3-dichloro-2-chloromethyl-2-methylpropane (11.0 g., b.p. 64–65° at 8 mm., n^{20}D 1.4837, d^{20}_4 1.264).

Methyl ether (1.5 g.) and polymethylene (0.02 g.) were obtained as in the carbon tetrachloride experiment. This experiment was repeated six times and quantities of 1,3-dichloro-2-chloromethyl-2-methylpropane ranged from 2.8 to 5.0 g., and those of methyl ether from 1.5 to 5.6 g. In one reaction of diazomethane (37.2 g.) with chloroform (480 g.), a careful search was made for intermediate products (1,1,1-trichloroethane, 1,2,2-trichloropropane and 1,2-dichloro-2-chloromethylpropane) and none were found.

The Reaction of Diazomethane with Methyl Trichloroacetate.—The reaction of diazomethane (9.3 g., 0.225 mole), swept over a period of 1.5 hours into methyl trichloroacetate (122 g., 0.84 mole) illuminated by a 150-watt projection photoflood lamp, was instantaneous. The heat of reaction raised the temperature of the reaction mixture to its boiling point. Nitrogen (7.6 l. S.T.P.) was evolved, but a careful search gave no methyl ether.

The reaction mixture was distilled through a 12-plate Fenske column. The unreacted methyl trichloroacetate was obtained in two distillate fractions: 1 (b.p. 50–51° at 14 mm., 57 g., n^{20}D 1.4572) and 2 (b.p. 51–51.6° at 14 mm., n^{20}D 1.4576). The distillation residue (14.6 g.) was then distilled through a Vigreux column. Three fractions were obtained: 1 (b.p. 54–57° at 1 mm., 4.79 g., n^{20}D 1.4800), 2 (b.p. 57–59° at 1 mm., 4.38 g., n^{20}D 1.4808) and 3 (b.p. 59–74° at 1 mm., 1.0 g.; n^{20}D 1.4858). A residue (3 g.) remained. Fractions 1 and 2 were shown to be methyl tris-(chloromethyl)-acetate (60% yield).

---

[16] B. Eistert, "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, New York, N. Y., 1948, p. 564.

[17] H. Hosaeus, *Ann.*, **276**, 76 (1901).

Anal. Calcd. for $C_6H_9O_2Cl_3$: Cl, 48.46. Found: Cl, 48.97.

This ester (1.3 g.) was added to an ether solution of lithium aluminum hydride (10 ml., 0.5 *N*), and 1,3-dichloro-2-chloromethyl-2-hydroxymethylpropane (0.86 g., m.p. 64–65°, m.p. of mixture with an authentic sample[5] 64–65°) was obtained. This alcohol (0.4 g.) was then treated (2-hr. reflux) with thionyl chloride (1.5 g.) and pyridine (0.4 ml.) to give 1,3-dichloro-2,2-bis-(chloromethyl)-propane (0.35 g., m.p. 97–98°, m.p. of mixture with an authentic sample[5] 97–98°).

The identification of the product ester by the above method was tried because of the difficulty of its hydrolysis to the known tris-(chloromethyl)-acetic acid. It was recovered unchanged from three attempted hydrolyses: (1) with 2 *N* hydrochloric acid in aqueous methyl alcohol (50%, 17 hr. reflux), (2) with concentrated sulfuric acid (solution kept for 12 hr., and then added to water) and (3) with concentrated nitric acid (25%) in concentrated H_2SO_4 (steam-bath for 0.5 hr.). Treatment with ammonium hydroxide in aqueous methanol (50%, reflux for 12 hr.) gave no reaction, and reaction with 4 *N* sodium hydroxide in the aqueous methyl alcohol gave only water soluble products.

The Reaction of Diazomethane with Methyl α-Bromopropionate.—Methyl α-bromopropionate (177 g., 0.94 mole, illuminated in the mercury coil apparatus) was treated with diazomethane (18.6 g., 0.45 mole) as described above. The color of the latter disappeared from the solution 15 minutes after its addition was complete. Distillation of the reaction mixture gave unreacted methyl α-bromopropionate (160 g., b.p. 55–57° at 19 mm., n^{20}_D 1.4464) and methyl β-bromoisobutyrate (16.6 g., b.p. 75–75.7° at 19 mm., n^{20}_D 1.4550, 20% yield).

Anal. Calcd. for $C_5H_9O_2Br$: Br, 44.13. Found: Br, 44.11.

The product ester (1.0 g.) was treated (8 days at room temp.) with hydrochloric acid (10%) in aqueous methyl alcohol (50%). β-Bromoisobutyric acid (0.2 g., m.p. 15–17°) was isolated.

The Reaction of Diazomethane with Ethyl Bromoacetate.—This reaction with diazomethane (9.3 g., 0.225 mole) and the ester (220 g., 1.44 moles) was conducted as described above. The diazomethane color disappeared 40 minutes after its addition was complete. The product, ethyl β-bromopropionate, could not be separated from the unreacted ethyl bromoacetate by fractional distillation through the 12-plate Fenske column. The reaction mixture was distilled to give a mixture of the two esters (210 g., n^{20}_D 1.4520). The distillation residue (21 g.) was distilled through a small Vigreux column to give a fraction (7 g., n^{20}_D 1.4533, b.p. 48–60° at 10 mm.) and a tarry residue (14 g.). This liquid fraction was partially hydrolyzed with hydrobromic acid (20%) in aqueous methyl alcohol (50%). Unreacted ester (5.5 g.) was obtained, and the acid isolated was subjected to chromatographic separation on a silicic acid (Eimer and Amend) column using a benzene–ligroin (50%) solution. The first acidic product eluted was β-bromopropionic acid (1.3 g., m.p. 60.5–61.5°, m.p. of mixture with authentic sample 61°).

Reaction Rate and Inhibition Studies.—In a dark room, diazomethane (9.3 g., 0.225 mole) was swept by a stream of nitrogen into carbon tetrachloride (250 g., 1.60 mole) cooled to −22° in the previously described, mercury coil reaction vessel. After addition was complete, the reaction vessel and its contents were held at 0° in an ice–water-bath contained in a large dewar flask. A slow evolution of nitrogen occurred (see Fig. 2, after 35 min., 40 ml.; 250 min., 345 ml.).

A reaction mixture containing diazomethane (9.3 g., 0.225 mole) and carbon tetrachloride (300 g., 1.95 moles) was prepared as described above. The reaction vessel was then immersed in an ice–water-bath in an unsilvered dewar flask, and a 150-watt spotlight (held at a distance of 1 ft.) was turned on the flask. The evolution of nitrogen with time is given in Fig. 2. In 35 minutes, 4,365 ml. of nitrogen was obtained; and when the reaction was complete (140 min.), 5,880 ml. had evolved.

A rate study of the light-induced reaction of diazomethane (9.3 g., 0.225 mole) with ethyl bromoacetate (220 g., 1.23 moles) was conducted as described above. 5,630 ml. of nitrogen was obtained in 35 minutes, and 8,210 ml. had evolved when the reaction was complete (105 min., see Fig. 2).

A solution containing diazomethane (9.3 g., 0.225 mole), diphenylamine (5.0 g., 0.03 mole) and carbon tetrachloride (200 g., 1.30 mole) was illuminated as above with the 150-watt spotlight. After 18 hours the loss of the yellow diazomethane color was incomplete. The solution was distilled at reduced pressure. A yellow liquid, presumably diazomethane (3 ml.) condensed in the −80° trap. It evaporated completely on warming, and the vapor was conducted into a solution of 3,5-dinitrobenzoic acid (1.5 g.) in ether. Methyl 3,5-dinitrobenzoate (1.5 g., m.p. 106–107°, m.p. of mixture with an authentic sample 106–107°) was obtained. The distillation residue gave no 1,3-dichloro-2,2-bis-(chloromethyl)-propane.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

1-Hydroxy-11-methoxychrysene[1]

BY RODERICK A. BARNES AND MICHAEL A. MANGANELLI[2]

RECEIVED MAY 29, 1952

Proof has been obtained that 4-methoxyphenanthrene undergoes the Friedel–Crafts reaction at the 1-position. The keto-acid obtained by using succinic anhydride in the reaction has been reduced, cyclized and dehydrogenated to yield 1-hydroxy-11-methoxychrysene.

In connection with work on the preparation of hydroaromatic compounds related to steroids it was desirable to have available the completely aromatic analogs which could be used as reference compounds for structure proof by dehydrogenation. 1-Hydroxy-11-methoxychrysene, a previously unknown chrysene derivative, was of interest for this purpose.

4-Methoxyphenanthrene (I) was chosen as the starting material with the expectation that a Friedel–Crafts reaction with succinic anhydride would introduce the desired four-carbon chain at the 1-position. Mosettig and Duval[3] have previously carried out a reaction between I and acetyl chloride and obtained a ketone, x-acetyl-4-methoxyphenanthrene (m.p. 122.5–123.5°) which was different from the ketone (y-acetyl-4-methoxyphenanthrene, m.p. 80–81.5°) obtained by a Fries rearrangement of 4-phenanthryl acetate followed by methylation.

The reaction of I with succinic anhydride produced a single ketoacid (II) in 95% yield; this indicated that reaction had taken place almost exclu-

---

[1] Presented at the Meeting-in-Miniature of the North Jersey Section of the A.C.S., January 28, 1952.

[2] Abstracted from a thesis submitted by M. A. Manganelli to the Graduate Faculty of Rutgers University for the Ph.D. degree, January, 1952.

[3] E. Mosettig and H. Duval, THIS JOURNAL, **60**, 2409 (1938).