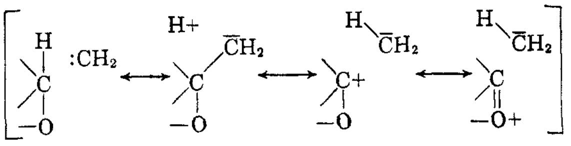
limits. Rearrangement of a hypothetically intermediate "ylid", urged so strongly by Meerwein and coworkers,[5] is therefore unimportant in the reaction of methylene with tetrahydrofuran and, presumably, with diethyl ether also.

The deviation from the statistical distribution in the reaction of methylene with the carbon-hydrogen bonds is small and lies in the direction of favoring the α-hydrogen atoms. Granting that the deviations are significant, one can rationalize their direction by comparing transition states of the type considered by Doering and Knox.[6] In the ethers, the transition state of reaction with the α-hydrogen could be favored by contribution of a resonance structure involving the oxygen atom.

It may be pointed out that appreciable carbon-rearrangement of the hypothetical diethyl ether–methylene "ylid" would have led to deviation in the opposite direction from that observed, whereas



hydrogen-rearrangement from such an "ylid" would have led to deviation in the observed direction.[7]

These quantitatively more reliable results in no way change those reported by Meerwein and co-workers.[1] The conclusions are perhaps best expressed in a negative way: There is no new phenomenon in the reaction of these two ethers with methylene to compel one to consider the possible intervention of an "ylid" intermediate. It should, however, be pointed out that there are far more compelling reasons to consider an intermediate "ylid" in reactions of ethyl diazoacetate.[4,5,8]

EXPERIMENTAL

Photochemical decomposition of diazomethane in diethyl ether. An ethereal solution of diazomethane was prepared from 105 g. of crude nitrosomethylurea and 11 g. of purified diethyl ether and dried over potassium hydroxide at 0°. Irradiation with two General Electric sunlamps at 15–17° caused the smooth evolution of nitrogen and complete decolorization of the solution in 18 hr. The bulk of the solvent was removed by distillation through a 2-ft. column packed with glass helices. Total distillation of the residue gave 18.1 g. of a colorless product of b.p. 50–72°. Analysis and separation by g.l.p.c. afforded diethyl ether, ethyl i-propyl ether, and ethyl n-propyl ether. The substances were identified by comparing the infrared spectra with those of authentic materials. The ratio of n-propyl to i-propyl ether, determined by area measurement and corrected for differences in sensitivity, was 1.25.

Authentic ethyl n-propyl ether was prepared from sodium propoxide and ethyl iodide in boiling propanol-1; b.p. 63–64°; n_D^{25} 1.3698. Ethyl i-propyl ether was prepared in a similar fashion: b.p. 53.5°; n_D^{25} 1.3624.

Photochemical decomposition of diazomethane in tetrahydrofuran. In the same manner as described above, the irradiation of diazomethane in tetrahydrofuran (purified by boiling under reflux over sodium and distilling) gave 30.2 g. of crude product; b.p. 85–115°. Separation by g.l.p.c. showed recovered tetrahydrofuran, 2-methyltetrahydrofuran, and 3-methyltetrahydrofuran. The ratio of the latter compounds was 1.26. Identification was by comparison of infrared spectra with those of authentic materials.

Samples of tetrahydropyran (b.p. 86°; n_D^{25} 1.4206) and 2-methyltetrahydrofuran (b.p. 80°; n_D^{25} 1.4052) were obtained commercially and refractionated. 3-Methyltetrahydrofuran was obtained by the sequence of reactions in which methylsuccinic acid was converted to the dimethyl ester, b.p. 195–197.5°, by ethereal diazomethane; the diester was reduced with lithium aluminum hydride to 2-methylbutandiol-1,4, b.p. 95–97°/1 mm.; and the diol was treated with 60% sulfuric acid in a sealed tube at 100° according to Yur'ev and Gragerov.[9] A pure sample isolated by g.l.p.c. had b.p. 85–87° (reported[8] 86–86.5°) and n_D^{25} 1.4012.

The question of the possible presence of tetrahydropyran was examined. The retention time of authentic tetrahydropyran is slightly longer than that of 3-methyltetrahydrofuran on a column of dioctylphthalate under the conditions we used. No peak or shoulder at this retention time was observed. To eliminate the possibility of smaller amounts having been formed, 3 cc. of the crude reaction product (containing about 10% tetrahydrofuran) was separated on a 5-ft., 2″ I.D., silicone-firebrick column into starting material, 2-methyltetrahydrofuran and 3-methyltetrahydrofuran. The last quarter of the 3-methyltetrahydrofuran peak was collected and its infrared spectrum was measured neat in a 0.025 mm. cell. The strong absorption band of tetrahydropyran at 873 cm.$^{-1}$ is useful for detecting small amounts of this material. There is a slight discrepancy at this frequency corresponding to *ca.* 2%. When 0.011 g. of tetrahydropyran was added to 1.1 g. of the reaction product (bulk of tetrahydrofuran removed) the band was easily identifiable in the final quarter of the 3-methyltetrahydrofuran band and corresponded in intensity to about 6%.

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Dimethyl Dithiolfumarate and Some Copolymerization Reactions[1]

C. S. MARVEL AND J. F. PORTER

Received September 24, 1958

Dimethyl dithiolfumarate (I) has been prepared from fumaric acid by the following series of reactions:

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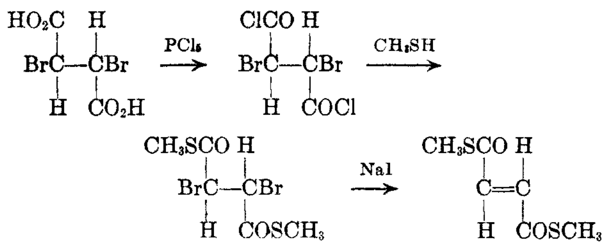
(1) This is a partial report of work done under contract with three Utilization Research and Development Divisions, Agricultural Research Service, U. S. Department of Agriculture, and authorized by the Research and Marketing Act. The contract was supervised by Dr. J. C. Cowan of the Northern Division.



I

The method used and the various steps are analogous to those used for making dialkyl thiolacrylate esters.[2]

Dimethyl dithiolfumarate could not be homopolymerized, but it does copolymerize with styrene and butadiene. No copolymerization with vinyl chloride could be achieved. The copolymerization of the dithiol ester with butadiene in the Mutual recipe[3] proceeded readily and with a charge ratio of 1 part of butadiene and 9 parts of dithiol ester, copolymer containing 7 parts of butadiene to 3 parts of dithiol ester was obtained.

Reactivity ratios were determined between the dithiol ester and butadiene and styrene using the standard procedures.[4] For dimethyl dithiolfumarate and butadiene, the values are $r_1 = -0.0014 \pm 0.027$ and $r_2 = 0.0106 \pm 0.0175$, respectively. For the dithiol ester and styrene, the values are $r_1 = 0.0163 \pm 0.013$ and $r_2 = 0.098 \pm 0.013$, respectively. It may be noted that the reactivity ratios for diethyl fumarate and styrene are $r_1 = 0.025 \pm 0.015$ and $r_2 = 0.21 \pm 0.02$[5] and for diethyl fumarate and butadiene are $r_1 = 0.25$ and $r_2 = 2.13$,[6] respectively.

EXPERIMENTAL

α,α′-Dibromosuccinyl chloride was prepared by adding bromine to sodium fumarate, converting the dibromo salt to the free acid and treatment of this with phosphorus pentachloride as described by Lutz.[7]

Dimethyl α,α′-dibromodithiolsuccinate. In a half-liter, three-necked, round-bottomed flask were placed 24 g. (0.5 mole) of methanethiol. To avoid the loss of the volatile mercaptan the flask was cooled in an ice bath and fitted with a condenser containing Dry Ice and acetone. Seventy grams (0.224 mole) of α,α′-dibromosuccinyl chloride was added dropwise to the thiol. When hydrogen chloride was no longer liberated, the reaction mixture was dissolved in ether and the solid was purified by three successive crystallizations from ether. Yield: 42 g. (56% based on the acid chloride), m.p. 171–172°.

Anal. Calcd.: C, 21.4; H, 2.3; Br, 47.6; S, 19.0. Found: C, 22.22; H, 2.70; Br, 43.68; S, 19.78.

Dimethyl dithiolfumarate. A solution of 20.3 g. of dimethyl α,α′-dibromodithiolsuccinate dissolved in 400 ml. of acetone was prepared. A second solution of 25 g. of sodium iodide dissolved in 300 ml. of acetone was placed in a one-liter, three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel. The stirrer was started, the first solution was added dropwise to the flask, and the mixture stirred for 4 hr. after the addition was complete. The precipitated sodium bromide was removed by filtration and the solution was concentrated on a steam bath to about one third of the original volume. Five hundred milliliters of ether was then added, and the mixture was washed with a 10% aqueous solution of sodium thiosulfate until all the color due to free iodine was removed. The ether was removed by distillation on a steam bath at atmospheric pressure until the first crystals appeared in the ethereal solution. The solution was allowed to cool to room temperature and then cooled in a Dry Ice–acetone bath. The unsaturated ester was removed by filtration and recrystallized from ether. Yield: 45%, m.p. 78–79°.

Anal. Calcd.: C, 40.9· H, 4.55; S, 35.9. Found: C, 40.61; H, 4.74; S, 36.04.

Dimethyl dithiolfumarate–butadiene copolymer. In a standard emulsion system a charge of 17.5 g. of 2.86% ORR soap solution in redistilled water, 0.024 g. of Hooker's lauryl mercaptan, 1.0 g. of butadiene, 9.0 g. of dimethyl dithiolfumarate, and 1 ml. of a 3% aqueous solution of potassium persulfate was used in the usual 4-oz. screw-cap polymerization bottle. Polymerization was allowed to proceed at 50° for 5 hr. with end-over-end agitation. The polymer was coagulated in the usual manner, washed thoroughly, dissolved in benzene, and reprecipitated by pouring into methanol. This was repeated three times. The polymer was then dried. Four runs gave yields of about 1.2–1.3 g. The inherent viscosities varied from 2.13–2.24 (0.25 g./100 ml. benzene at 25°).

Anal. Found: C, 74.03; H, 8.92; S, 12.17.

This corresponds to a ratio of 7 parts of butadiene to 3 parts of dimethyl dithiolfumarate in the copolymer.

Reactivity ratios. The method of Mayo and Lewis[4] was followed. Benzene was used as the solvent and benzoyl peroxide as the initiator. Conversion was less than 5% in every case. The experimental data for the reactivity ratios of the ester with butadiene is given in Table I and with styrene in Table II.

TABLE I

DATA USED IN CALCULATION OF REACTIVITY RATIOS OF STYRENE AND DIMETHYL DITHIOLFUMARATE

	Charge			Product		
Sample	Dimethyl dithiolfumarate, g.	Styrene, g.	$\frac{M_1}{M_2}$[a]	% S	% C	$\frac{m_2}{m_1}$[b]
1	0.2222	1.7371	0.0755	15.30		2.3332
2	0.2335	3.5551	0.04102	12.40		3.2747
3	3.8237	2.3573	0.9585		60.86	1.0756
4	3.9069	0.8510	2.7133		60 29	1 0274
5	1.1866	2.5638	0.2735		63.92	1.3758
6	4.2684	0.8981	2.8074		60.06	1.0080

[a] $\frac{M_1}{M_2}$ = mole ratio, dimethyl dithiolfumarate/styrene in the charge. [b] $\frac{m_2}{m_1}$ = mole ratio, styrene/dimethyl dithiolfumarate in the product.

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TABLE II

Data Used for the Calculation of Reactivity Ratios of Dimethyl Dithiolfumarate and Butadiene

	Charge			Product	
Sample	Dimethyl dithiolfumarate, g.	Butadiene, g.	$\frac{M_1}{M_2}$[a]	% C	$\frac{m_2}{m_1}$[b]
1	1.2695	1.2598	0.3092	52.47	1.0387
2	1.1694	0.7241	0.4950	53.03	1.0610
3	1.3908	0.8747	0.4879	52.31	1.0199
4	1.4841	0.1954	2.3308	52.18	1.0058
5	1.0563	0.4652	0.6968	52.04	1.9885

[a] $\frac{M_1}{M_2}$ = mole ratio, dimethyl dithiolfumarate/butadiene in the charge. [b] $\frac{m_2}{m_1}$ = mole ratio, butadiene/dimethyl dithiolfumarate in the product.

The data thus obtained were plotted and calculated in the usual manner.

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Reaction of Dichlorocarbene with Conjugated Dienes[1]

Milton Orchin[2] and E. C. Herrick[3]

Received October 6, 1958

A recent article[4] describing the addition of dihalocarbenes to 1,3-butadiene prompts us to report similar work which has been in progress for several years. Our results corroborate the published work; addition to butadiene occurs almost exclusively at the 1,2-position. In addition to the expected 1,1-dichloro-2-vinylcyclopropane, a compound with properties consistent with the structure of 2,2,2′,2′-tetrachlorobicyclopropyl was isolated; its formation can be explained by 1,2- and 3,4- double addition of the dichlorocarbene.

We wish to report here in detail our experiments with isoprene. 1,2-Addition to this unsymmetrical diene could lead to two different products. Structural information was secured as follows: After treatment of the isoprene with chloroform in the presence of potassium isopropoxide, the product was dechlorinated with sodium in liquid ammonia containing methanol. The hydrocarbon mixture was recovered and saturated with hydrogen. Mass spectra analysis of the saturated hydrocarbons showed that the product was principally that resulting from 1,2-addition to the substituted double bond of isoprene; small amounts of material corresponding to addition at the other double and some evidence for 1,4-addition were also found, although evidence for the 1,4-addition was inconclusive.

EXPERIMENTAL[5]

Experiments with Butadiene. 2,2,2′,2′-Tetrachlorobicyclopropyl. Reaction of butadiene with chloroform in the presence of sodium *tert*-butoxide gave the known[4] 1,1-dichloro-2-vinylcyclopropane. After its removal by distillation, the residue was distilled *in vacuo* and a fraction b.p. 76° (6 mm.) was collected which on crystallization from pentane had m.p. 79.5–80.5°.

Anal. Calcd. for C_6H_6Cl: Cl, 64.5; C, 32.7; H, 2.7. Found: Cl, 64.1; C, 33.0; H, 2.6.

The infrared spectrum showed bands at 3430, 2940, 1049, 1011, and 986 cm^{-1}. Such bands are consistent with the presence of cyclopropyl groups.[6]

1,1-Dichloro-2-ethylcyclopropane. A solution of 0.553 g. of 1,1-dichloro-2-vinylcyclopropane in 15 ml. of cetane was treated with hydrogen at atmospheric pressure in the presence of a reduced platinum catalyst (Houdry Type 3). Absorption of 1.10 moles of hydrogen per mole of compound occurred rapidly. Careful fractionation gave a forerun and then the bulk of the material distilled at 121°. Chlorine analysis indicated impurities present. In subsequent work a substantial quantity of 1,1-dichloro-2-ethylcyclopropane was isolated from the carbene reaction using sodium *tert*-butoxide. Possibly some sodium failed to react with the alcohol and during the work-up, sodium reduction of a portion of the 1,1-dichloro-2-vinylcyclopropane occurred. Careful fractionation gave material, b.p. 120°, n_D^{20} 1.4497, d_4^{20} 1.1171.

Anal. Calcd. for $C_4H_8Cl_2$: Cl, 51.0; C, 43.2; H, 5.8. Found: Cl, 51.0; C, 42.9; H, 5.8.

Experiments with Isoprene. 1,1-Dichloro-2-methyl-2-vinylcyclopropane. After the addition of 50 g. (1.25 moles) of potassium to 600 ml. of isopropyl alcohol (distilled from sodium) and complete disappearance of the potassium, the excess alcohol was removed by distillation. The potassium isopropoxide was dried overnight under reduced pressure at 100°. The salt was suspended in 200 ml. of petroleum ether and 150 ml. (1.5 moles) of isoprene (Philips Petroleum Company, 99%) was added. There was then added dropwise with stirring at 0°, about 150 g. (1.25 moles) of chloroform. There appeared to be an immediate reaction. The reaction mixture was stirred at 0° for 2 hr. after addition was complete, and the mixture was then poured into water. The organic phase was separated, washed with water, dried over anhydrous sodium sulfate, and the solvent was evaporated. The residue was distilled through a short helix-packed column to give two fractions the first of which was a forerun, 3.9 g., b.p. 60° (33 mm.). The second fraction had b.p. 64° (33 mm., 24.5 g.). This material reacted very slowly with potassium permanganate solution; there was almost no reaction with bromine water.

Anal. Calcd. for $C_6H_8Cl_2$: Cl, 46.9, M_D calcd. 37.4 (including the value 0.6 for the cyclopropane ring[7]). Found: Cl, 46.5; M_D, 37.8.

The infrared spectrum gave strong bands at 2985, 1640, 1440, 1100, 1088, 1051, 1026, 994, and 950 $cm.^{-1}$.

The same reaction was repeated on a large scale in a 5-gal.,

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[1] Presented before the Second Delaware Valley Meeting, ACS, February 5, 1958.

[2] Department of Chemistry, University of Cincinnati.

[3] Research Division, Houdry Process Corporation; present address, Climax Molybdenum Laboratories, Detroit, Mich.

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[5] Melting and boiling points uncorrected. We wish to thank the following members of the Houdry staff: A. Juliard and C. G. Harriz for all the microanalysis, A. Wheeler for the hydrogenation experiments, J. Terrell for the mass spectra analyses, and Paul Work and Earle Creamer for the infrared analyses.

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[7] V. A. Slabey, *J. Am. Chem. Soc.*, **76**, 3603 (1954).