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]

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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′-Tetrachlorobicyclo propyl. 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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(4) R. C. Woodworth and P. S. Skell, *J. Am. Chem. Soc.*, **79**, 2542 (1957).

(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.

(6) V. A. Slabey, *J. Am. Chem. Soc.*, **76**, 3603 (1954).

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

glass-lined kettle using a high-dilution technique[8,9] in which isoprene was used as solvent. To 3 gal. of *tert*-butyl alcohol which had been distilled from sodium carbonate, there was added 9.1 gram atoms of sodium. After the sodium had reacted, the excess alcohol was removed and the residual butoxide was dried at 60° in vacuo. The salt was suspended in 7 liters of isoprene and 9 moles of chloroform was added during 5.5 hr. at a slurry temperature of about 0°. The reaction product was isolated in the usual manner and fractionally distilled. The fractions b.p. 145° and with a constant refractive index (n_D^{20} 1.4787) were combined. Vapor fractometer analysis indicated a purity of about 96%. The yield of pure 1,1-dichloro-2-methyl-2-vinylcyclopropane based on sodium was 37.2%.

1-Methyl-1-vinylcyclopropane. To a mixture of 15.1 g. (0.1 mole) of 1,1-dichloro-2-methyl-2-vinylcyclopropane in 50 ml. of methanol and 100 ml. of liquid ammonia there was added portionwise 9.4 g. (0.4 mole) of sodium. As soon as the first few pieces were added, sodium chloride began to precipitate. The sodium dissolved rapidly with a transient blue color. Gradually the rate of reaction of the sodium decreased and at the completion of the addition of the 9.4 g. of sodium, there appeared to be an excess of sodium present. The ammonia was allowed to evaporate at room temperature. Unfortunately, most of the hydrocarbon was lost during the spontaneous evaporation of the ammonia. About 10 ml. of methanol was added followed by sufficient water to dissolve the salts. The small hydrocarbon layer was separated, washed with water, and filtered through calcium chloride. The product (one gram) had n_D^{25} 1.432 and gave a positive test for unsaturation with bromine water. Mass spectrographic analysis indicated the presence of 1-methyl-1-vinylcyclopropane, contaminated with a small quantity of other material.

1-Methyl-1-ethylcyclopropane. To 0.7031 g. (0.0094 mole) of the above impure 1-methyl-1-vinylcyclopropane there was added about 50 ml. cetane and 0.5 g. Type III Houdry catalyst (Pt on Al_2O_3). The sample was hydrogenated at 26° and one atmosphere of hydrogen. The rate of hydrogen uptake was constant at 4.2 ml./min. until 220.7 ml. was absorbed, then decreased to 0.6 ml./5 min. The uptake of 220.7 ml. of hydrogen corresponds to 1.03 moles per mole of 1-methyl-1-vinylcyclopropane. The reduced product was distilled through a microcolumn and 0.5 g. of distillate collected. Mass spectrographic analysis indicated the following hydrocarbons were present in the mole percentages given:

COMPOUND	MOLE %
3-Methylpentane	11.3
2,2-Dimethylbutane	1.9
2-Methylpentane	4.7
2,3-Dimethylbutane	
1-Ethyl-1-methylcyclopropane	74.3
Isopropylcyclopropane	3.4
Methylcyclopentane	4.4

The presence of the last two compounds was inferred on the basis of an excess at mass 39 and deficiencies at 55, 69, and 84 after the other components had been accounted for. The evidence for 1,4-addition leading to methylcyclopentane must accordingly be considered inconclusive at the present time.

2,2-Dichloro-1-methylcyclopropane-1-carboxylic acid. To 10.8 g. (0.071 mole) of 1,1-dichloro-2-methyl-2-vinylcyclopropane in 100 ml. of acetone there was added 2 g. of sodium bicarbonate. The mixture was cooled to 0° and 39 g. of potassium permanganate was added with stirring over about 4 hr. The mixture was poured into a beaker, the acetone was allowed to evaporate, and the residue was treated with solid sodium bisulfite and dilute sulfuric acid until the mixture was colorless. The reaction mixture was extracted with ether, and the ether extract was shaken with sodium bicarbonate solution. The sodium bicarbonate solution was acidified with dilute hydrochloric acid. The acid mixture was extracted with ether, and the ether solution was dried and distilled at 1 mm. The product boiling at 110° (1 mm.) amounted to 6.0 g. and crystallized on standing, m.p. 61°. The crude product was recrystallized twice from pentane to give white clusters of crystals, m.p. 60–62°.

Anal. Calcd. for $C_5H_6O_2Cl_2$: Cl, 42.0. Neut. equiv. 169. Found: Cl, 41.7. Neut. equiv. 173.5.

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