

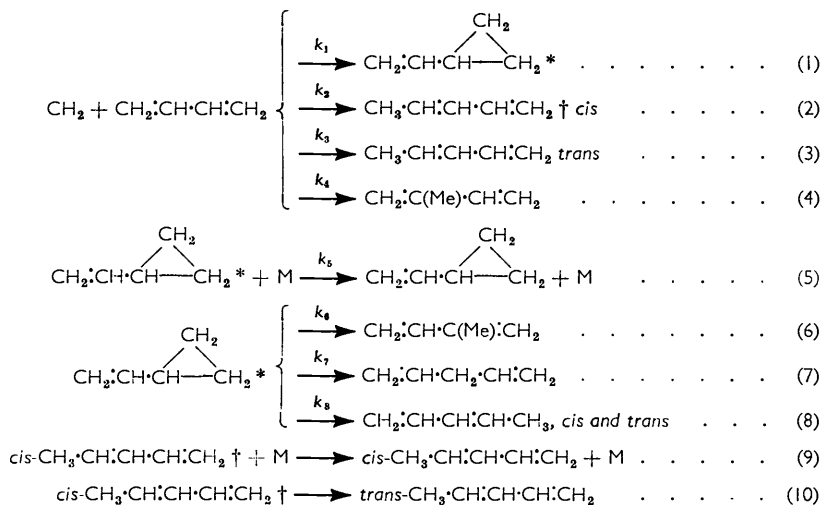
866. *The Reaction of Methylene with Buta-1,3-diene.*

By BARBARA GRZYBOWSKA, J. H. KNOX, and A. F. TROTMAN-DICKENSON.

Methylene (from the photolysis of keten and diazomethane) reacts with buta-1,3-diene by (i) insertion into the C-H bonds and (ii) addition to form vinylcyclopropane. At low pressures the vinylcyclopropane isomerizes by fission of the C-C bond β to the double bond. The isomerization, unlike that of the alkylcyclopropanes, goes little beyond 50% completion. It is suggested that this behaviour is associated with the formation of electronically excited vinylcyclopropane.

THE combination of methylene with a hydrocarbon to yield a cyclopropane or cyclobutane derivative is so exothermic that the resultant molecule is chemically activated and will either isomerize or decompose unless it loses its excess of energy. The products are similar to those formed when cyclanes, activated by thermal collisions, react. This pattern of behaviour has been observed for cyclopropane¹ from ethylene,² methylcyclopropane³ from propene^{4,5} and cyclopropane,^{4,6} 1,1-dimethylcyclopropane⁷ from isobutene,⁸ 1,2-dimethylcyclopropane⁹ from but-2-ene,¹⁰ and methylcyclobutane¹¹ from cyclobutane.¹² The object of the present work was to study the reactions of vinylcyclopropane activated by the exothermicity of the addition of methylene to buta-1,3-diene. The thermal isomerization of vinylcyclopropane probably cannot be investigated because at the necessary high temperatures side reactions are bound to interfere. This is the first example of the study of a reaction by synthetic activation that could not be conventionally investigated.

The following reaction scheme was expected by analogy with similar systems:



¹ Chambers and Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399; Corner and Pease, *ibid.*, 1945, **67**, 2067; Pritchard, Sowden, and Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, *A*, **217**, 563; Rabinovitch, Schlag, and Wiberg, *J. Chem. Phys.*, 1958, **28**, 504; Falconer, Hunter, and Trotman-Dickenson, *J.*, 1961, 609.

² Frey, *J. Amer. Chem. Soc.*, 1957, **79**, 1259; Frey and Kistiakowsky, *ibid.*, p. 6373.

³ Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277.

⁴ Knox and Trotman-Dickenson, *Chem. and Ind.*, 1957, 1039.

⁵ Butler and Kistiakowsky, *J. Amer. Chem. Soc.*, 1960, **82**, 759.

⁶ Butler and Kistiakowsky, *J. Amer. Chem. Soc.*, 1961, **83**, 1324.

⁷ Flowers and Frey, *J.*, 1959, 3953.

⁸ Wells, Knox, and Trotman-Dickenson, *J.*, 1958, 2897; Frey, *Proc. Roy. Soc.*, 1959, *A*, **250**, 709.

⁹ Frey, *Proc. Roy. Soc.*, 1960, *A*, **257**, 122; 1961, *A*, **260**, 424.

¹⁰ Frey, *Proc. Roy. Soc.*, 1959, *A*, **251**, 579.

¹¹ Das and Walters, *Z. phys. Chem. (Frankfurt)*, 1958, **15**, 22.

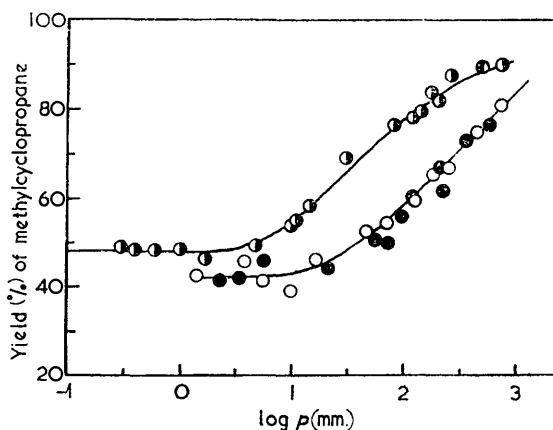
¹² Frey, *Trans. Faraday Soc.*, 1960, **56**, 1201.

The asterisk and dagger indicate that there is evidence that the designated molecules are activated.

In accordance with this scheme, it is found that when keten is photolysed in a Pyrex reaction vessel above 500 mm. pressure, the products are: vinylcyclopropane, 90.0%; penta-1,4-diene, 1.6%; isoprene, 2.4%; *cis*-penta-1,3-diene, 2.4%; and *trans*-penta-1,3-diene, 3.6%. These figures were obtained on the assumption that equal amounts of each hydrocarbon yielded equal peak areas on the recorder fed from the thermal conductivity gauge of the chromatographic system, which is probably correct within 1–2%. Since penta-1,4-diene can arise only by isomerization of vinylcyclopropane its amount should be added to that of the cyclic compound in order to calculate the relative reactivity of C–H and C=C double bonds. Hence we find that (Reactivity C=C)/(Reactivity C–H) = 33. There is little difference in the reactivities of the central and terminal C–H bonds. The relative reactivities of the double and the single bond in C=C–H depend considerably upon the source and wavelength of actinic light used to produce the methylene. Results of different workers on different systems cannot be readily compared, but it appears that the conjugation slightly activates the double C=C bond relative to the vinyl C–H bond.

FIG. 1. Variation, with pressure, of yield of vinylcyclopropane on addition of methylene to buta-1,3-diene.

- Methylene from keten, Pyrex vessel.
- Methylene from diazomethane, Pyrex vessel.
- Methylene from diazomethane, quartz vessel.



Below 500 mm. pressure the yield of vinylcyclopropane declines as shown in Fig. 1. At first the decline is similar to that found in the addition of methylene to other olefins and a plot of the reciprocal of the pressure against

$$\frac{\text{Proportion of vinylcyclopropane isomerised}}{\text{Proportion of vinylcyclopropane deactivated by collision}} = \frac{k_6 + k_7 + k_8}{k_5[M]}$$

yields the predicted straight line (Fig. 2) when the methylene is derived from the photolysis of keten and of diazomethane.

Hence $(k_6 + k_7 + k_8)/k_5 = 0.03$ (keten) and 0.058 (diazomethane) atm.⁻¹. As can be seen from the Table these results are in good agreement with what might be expected for a

The relative rates of reaction of cyclanes.

Compound	Thermal isomn., 10 ⁴ k (sec. ⁻¹), at 475°	k(isomn.)/k(deactivn.) * (atm. ⁻¹): CH ₂ from CH ₂ :CO	CH ₂ N ₂	Ref.
Cyclopropane	1.1	1.19	—	1, 2
Methylcyclopropane	2.8			3
from cyclopropane		0.284	0.44	5
from propene		0.06	0.120	6
1,1-Dimethylcyclopropane	5.7	0.003	0.02	7, 8
1,2-Dimethylcyclopropane	2.9	—	0.02	9, 10
Vinylcyclopropane	—	0.03	0.06	This work
Methylcyclobutane	31	0.05	0.25	11, 12

* The values of $k(\text{isomerization})/k(\text{deactivation})$ are sometimes not known to better than $\pm 30\%$.

cyclopropane derivative containing five carbon atoms which is rather more reactive than the alkyl-substituted compounds.

The yield of isoprene remains constant throughout our pressure range (Fig. 3). Presumably it is only formed in the initial addition of methylene to the olefin, and reaction 6 is negligible. Evidently vinylcyclopropane isomerizes only by mechanisms that involve the rupture of the C-C bond β to the double bond. This preferred rupture can readily be understood if the primary step is formation of a biradical by direct rupture. This would lead to a stable allylic radical on rupture of the β bond but not on rupture of the γ -bond. The observation provides some support for the mechanism of cyclopropane isomerization favoured by Rabinovitch and his co-workers.¹

The most striking observation is the limit below which the proportion of vinylcyclopropane in the products never falls. No other system has been found to exhibit this behaviour. That the limit is real is clearly shown in Fig. 1. It appears that there is a slight difference in the limits for methylene derived from keten and from diazomethane.

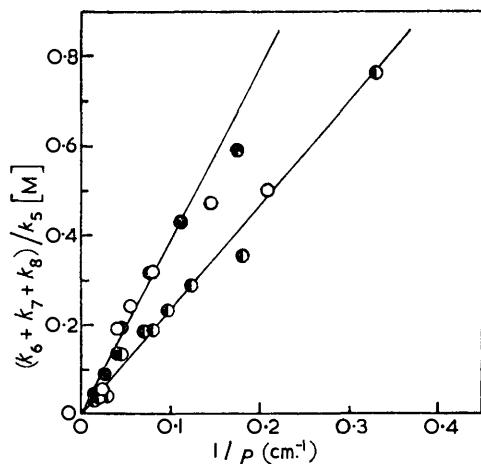


FIG. 2. Relative rates of isomerization and deactivation of activated vinylcyclopropane as a function of pressure. For open, full, and half-full circles see Fig. 1.

The phenomenon is probably connected with the presence of the vinyl group; no other unsaturated cyclopropane derivative has been investigated. The exothermicity of the methylene addition is so great that an electronically excited state of a compound containing π -electrons could be formed. The electronically excited molecule might then either lose energy by fluorescence, or be deactivated by collision, provided that its lifetime, with respect to isomerization, is long. Approximately half the adducts do not isomerize; possibly these molecules are formed in an electronically excited state either from the singlet or from the triplet methylenes released on photolysis.

The results shown in Fig. 3 also show that the *cis*-penta-1,3-diene is initially activated. At low pressures it isomerizes to the *trans*-compound before it is deactivated, despite the lower free energy of formation of the *cis*-compound at room temperature. It is possible that for such activated molecules the free energy of formation at very high temperatures is the relevant quantity. Above 1300° K the *trans*-compound is the more stable.

Experimental.—Pyrex and quartz reaction vessels of between 20 and 5000 c.c. were attached to a conventional high-vacuum system. They were kept slightly below room temperature by water streaming over them. The light source was an unfiltered 125 w medium-pressure mercury arc.

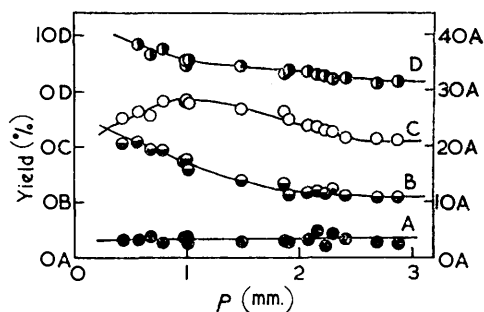


FIG. 3. Yields of isoprene ●, penta-1,4-diene ◐, *cis*-penta-1,3-diene ○, and *trans*-penta-1,3-diene ◑ from the photolysis of keten with buta-1,3-diene in a Pyrex vessel at room temperature.

Butadiene sulphone (dihydrothiophen dioxide) was thermally decomposed to butadiene and sulphur dioxide which was absorbed by 20% aqueous potassium hydroxide and in several bulb-to-bulb distillations over solid potassium hydroxide. Methylene was generated from keten and from diazomethane. Keten was prepared by the pyrolysis of acetic anhydride and purified by bulb-to-bulb distillation. Diazomethane was made by reaction of potassium hydroxide in ethylene glycol on *N*-methylnitrosourethane and was swept by a stream of nitrogen through a potash tube and a coil cooled in ice-salt into a trap cooled in liquid nitrogen. No impurities could be detected by gas chromatography.

The products were analysed by gas chromatography with hydrogen as the carrier gas at the optimum flow rate of 45 c.c. min.⁻¹ and a 20 ft. coil of copper tubing, cooled in ice, packed with 5% squalane-Celite (80—100 mesh). The detector was a thermal conductivity cell with tungsten filaments. Products were identified by comparison of their retention times, on different column packings, with known samples (when these were available) and by infrared spectroscopy.

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