oil. All attempts at crystallization failed even though the material appeared homogeneous by vpc and showed the expected spectroscopic properties. In contrast to the other olefins synthesized, this material was especially prone to thermal and base-catalyzed rearrangement. The homogeneous clear oil showed: exact mass, 232.1249 observed *vs.* 232.1251 calculated; ir (neat) 3.27 (m), 6.23 (m), 6.69 (m), 6.91 (m), 9.18 (m), 9.28 (m), 9.38 (m), 9.67 (m), 11.80 (m), 12.20 (m), 12.60 (m), 13.20 (s), 13.80 (s), 14.35 (s) μ; nmr (CCl_4) τ 2.82 (10 H, mult), 3.82 (1 H, mult), 4.38 (1 H, quartet), 5.45 (1 H, mult), 8.00 (1 H, mult), 8.92 (1 H, quartet, J = 4, 8 Hz), 9.40 (1 H, triplet, J = 4 Hz).

Direct Irradiation of 5,5-Diphenylcyclohexadiene (7). A degassed stirred solution of 0.40 g of 5,5-diphenylcyclohexadiene in 75 ml of cyclohexane was irradiated for 9 hr through quartz with a bank of 16 RPR 2537-Å lamps (New England Ultraviolet Co.). The vpc (5 ft × $^1/_8$ in., 5% SE-30 on Aeroport 30) indicated greater than 97% conversion of starting material and the formation of one major product in greater than 80% yield as determined by vpc integration. Isolation of the product by chromatography on neutral alumina yielded a colorless oil which readily polymerized on standing at room temperature. The nmr showed τ 2.77 (s, 10 H), 2.83–3.33 (mult partly obscured by aromatic absorption, 2 H), 3.83–4.16 (mult, 2 H), and 4.48–5.00 (mult, 2 H).[34]

In a second experiment, 0.40 g of 5,5-diphenyl-1,3-cyclohexadiene in 75 ml of cyclohexane was irradiated identically as described above. The crude photolysis mixture was then hydrogenated using 0.10 g of platinum oxide as catalyst (36 psi at room temperature for 21 hr). The yield of 1,1-diphenylhexane by vpc was 82%. The vpc-purified material showed an identical retention time and ir and nmr spectra with authentic material.[35]

Quantum Yield for Disappearance of 7 at 2537 Å. The quantum yield for diene disappearance was measured by irradiating 10 ml of about 1.7 × 10^{-5} *M* 7 in purified cyclohexane in quartz test tubes using four RPR 2537-Å lamps in a merry-go-round apparatus. The solution was purged with purified nitrogen prior to irradiation and the sample was sealed. Potassium ferrioxalate[36] actinometry gave light intensities on the order of 6.5 × 10^{-3} mE/(min)(10 cm^3). The solution was analyzed by flame ionization vpc (12 ft × $^1/_8$ in. column, 5% Carbowax 20M on 60–80 mesh Chromosorb G at 180°) using 2-acetonaphthone as standard. For good precision it was necessary to calibrate the instrument immediately prior to analysis with known mixtures of diene 7 and 2-acetonaphthone. The results of these studies are given in Table I.

Quantum Yields for Sensitized Reactions of 7. The quantum yields for the sensitized reactions of 7 were conducted with 350-nm light from a Bausch and Lomb high intensity grating monochromator (front and back slits at 5.0 mm). The cylindrical photolysis cell contained two identical compartments, each 4.5 cm in diameter with a 5-cm optical path. The cell was constructed from 4.5-cm Pyrex tubing and had optical quartz faces and a quartz spacer which separated the two compartments. In addition, each cell compartments was equipped with a $^{14}/_{20}$ ₸ male joint and a $^{6}/_{25}$ female joint for a thermometer.

Quantum yield determinations consisted of two irradiations. First, with potassium ferrioxalate in both compartments the material was irradiated and the ferrous ion concentration in the actinometer measured. Typical values of light intensity were on the order of 7.9 × 10^{-3} mE/(min)(65 ml). The second irradiation was carried out with the sample in the first cell and a fresh solution of potassium ferrioxalate in the back cell. Typical concentrations of diene 7 and sensitizer were 9.4 × 10^{-3} and 12.8 × 10^{-3} *M*. With this concentration of sensitizer, less than 1% of the incident irradiation was transmitted to the back cell. After irradiation of the magnetically stirred, nitrogen-purged, photolysis solution, the assay for starting material and product was made by vpc using 2-acetonaphthone as standard. As in the case of the direct excitation, calibration of the vpc using known mixtures of diene and internal standards immediately prior to analysis was necessary to obtain good results. The results of these measurements are given in Table III.

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[34] Our material shows an nmr spectrum identical with the material reported by Zimmerman and Epling.[1b]

[35] The authentic sample was synthesized by the reaction of 2 equiv of phenylmagnesium bromide with methyl hexanoate followed by dehydration of the resulting tertiary alcohol with a trace of *p*-toluenesulfonic acid in benzene. The resulting olefin was then hydrogenated with platinum oxide catalyst to the known 1,1-diphenylhexane.

(36) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. London*, **235**, 518 (1956).

Dimerization of Chloroprene and Related Dienes

Clare A. Stewart, Jr.

Contribution No. 247 from the Elastomer Chemicals Department,
Experimental Station, E. I. du Pont de Nemours and Company, Inc.,
Wilmington, Delaware 19898. *Received November 30, 1970*

Abstract: From the rates and products obtained in thermal dimerizations of chloroprene and other dienes, it is proposed that two mechanisms are operative—one which is probably concerted and electrocyclic in nature, requiring at least one cisoid diene unit, and leading to vinylcyclohexenes, the other diradical in nature, leading largely to divinylcyclobutanes, and appreciable only when favorable substitution is present.

Wheland and Bartlett have recently reported an apparent instance of simultaneous biradical 1,2- and concerted 1,4-cycloadditions to cyclopentadiene.[1] We wish to report some dimerizations of dienes which provide further information about such competition. This investigation was orginally undertaken to resolve apparent conflicts between the results of Robb and coworkers[2,3] and reports by previous workers[4-6] and observations in this laboratory concerning the products of dimerization of chloroprene (2-chloro-1,3-butadiene). Several related dimerizations have been included to verify the apparent significance of the results with chloroprene.

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(1) R. Wheland and P. D. Bartlett, *J. Amer. Chem. Soc.*, **92**, 3822 (1970).

(2) N. C. Billingham, P. A. Leeming, R. S. Lehrle, and J. C. Robb, *Nature* (*London*), **213**, 494 (1967).

(3) N. C. Billingham, J. R. Ebdon, R. S. Lehrle, J. L. Markham, and J. C. Robb, *Trans. Faraday Soc.*, **65**, 470 (1969).

(4) (a) W. C. Carothers, I. Williams, A. M. Collins, and J. E. Kerby, *J. Amer. Chem. Soc.*, **53**, 4211 (1931); (b) J. G. T. Brown, J. D. Rose, and J. L. Simonsen, *J. Chem. Soc.*, 101 (1944); (c) A. L. Klebanskii and M. M. Densisova, *Zh. Obshch. Khim.*, **17**, 703 (1947).

(5) A. C. Cope and W. R. Schmitz, *J. Amer. Chem. Soc.*, **72**, 3056 (1950).

(6) I. N. Nazarov and I. A. Kuznetsova, *Zh. Obshch. Khim.*, **30**, 134 (1960).

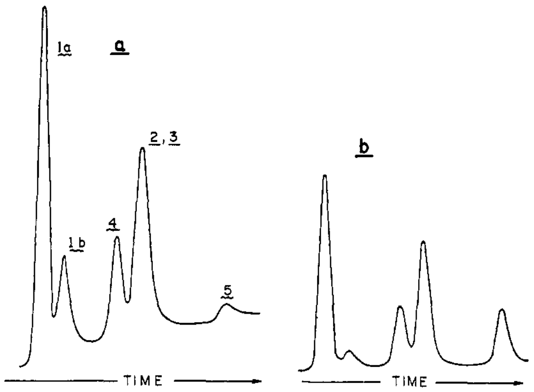
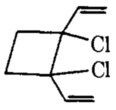
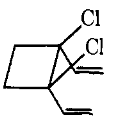


Figure 1. SE-30 chromatograms, chloroprene dimers (sample size varied for similar dimer content): (a) low conversion, (b) high conversion.

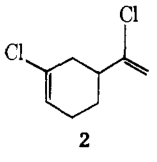
It was indicated[2,3] that chloroprene dimerization proceeds at room temperature with formation of only four isomers, the head-to-head divinylcyclobutane adducts **1a** and **1b**, and the Diels–Alder adducts, **2** and **3**, in which the unsubstituted vinyl group of the monomer serves as dienophile, with a 2:1 ratio of cyclobutanes to cyclohexenes. Various workers have indicated the presence of allylic halides suggested to be **4** and/or **4a** and various dehydrochlorination products, although these have not been rigorously characterized, nor has it been shown that they are original products rather than secondary derivatives resulting from thermal treatment of the original products. Cope and Schmitz[5] have conclusively demonstrated the structure of 1,6-dichloro-1,5-cyclooctadiene (**5**), isolated after prolonged heating.



1a



1b



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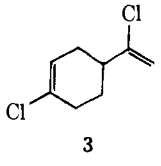

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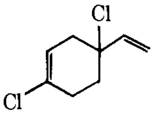

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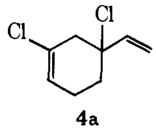
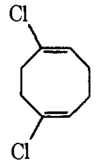


4a



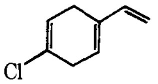
5

Results

Using temperature-programmed gas chromatography under the mildest conditions compatible with resolution, the initial products of dimerization at room temperature are found to contain about 15% each of **2** and **3** as claimed, but to include about 13% **4** in addition to **1a** and **1b** (41, 16%). Further, as reaction proceeds, the fraction of **1b** in the mixture is seen to decrease synchronously with the appearance and increase of an additional component, **5**, as indicated by typical tracings shown in Figure 1. With the exception of **1b**, each of these compounds was found to survive fractionation at low pressure and could be passed through the chromatograph under conditions of analysis without change. Infrared and proton magnetic resonance spectra of mixed isomers isolated without exposure to heat were in agreement with chromatographic analysis and the spectra of distillation fractions. No major change in spectral properties resulted when the mixture was heated briefly to 100° or passed preparatively through the chromatograph. From the combined results of fractionation, spectral examination, chromatography under several different conditions, and examination of thermal conversions of the isomers present (see below), it is believed that no other products are present in room temperature dimerization in an amount greater than 1% of the mixture. Quantitative data are reported only for experiments in which polymer formation was neglibible, but no difference in rate or products of dimerization was observed in instances where inhibition was not completely effective.[7]

The identity of **1b** is based solely on its isomerization to **5**. As discussed below, the rate of this process is in agreement with expectation based on the behavior of **1a** and of the unsubstituted analogs.[8,9] The structure of **5**, which was isolated by distillation as a low-melting solid, follows from its ozonolysis to dialdehyde and diacid chloride.[5] A mixture of **2** and **3** was obtained by redistillation of fractionation cuts containing **2**, **3**, and **4** after treatment with piperidine to remove the latter. These isomers were separated analytically only under much more rigorous chromatographic conditions. The earlier eluting isomer, which is slightly in excess at room temperature, is assigned structure **2** on expectation from symmetry and hydrolysis experiments by Nazarov,[6] who obtained somewhat more 3-acetylcyclohexanone than the corresponding 4-isomer. As described in the Experimental Section, the mixture was converted to chlorinated isomers of 4-ethynylcyclohexene and 4-acetylcyclohexene, the latter apparently identical with the product obtained from chloroprene and methyl vinyl ketone, but successful resolution of chlorine isomers was not achieved.

When heated, fractions containing **4** evolved HCl at variable, apparently autocatalytic rates, with formation of two lower boiling dehydrochlorination products. The intermediate product is tentatively identified as 1-vinyl-4-chloro-1,4-cyclohexadiene (**6**), on the basis of its nmr spectrum. Purified **6** was relatively stable to heat but was isomerized in the presence of acid to the other degradation product, **7**, identified as 4-chloroethylbenzene by comparison to an authentic sample.[10]



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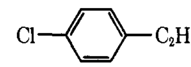

7

Isomer **1a**, obtained by fractional distillation or preparative chromatography, solidified on cooling, mp −28 to −26°. The infrared spectrum agreed with that published[2] except for the absence of the "trace aromatic impurity" absorption at 1500 cm^{-1}. The latter is characteristic of **5**, and it is probable that the sample obtained by Robb contained some cis isomer, **1b**, which had partially isomerized before or during spectral anal-

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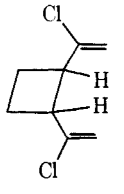
(7) Conflicting observations which have been reported do not appear to be generally applicable and probably apply only to very specific conditions. See P. A. Leeming, R. S. Lehrle, and J. C. Robb, S. C. I. Monograph, Society of Chemical Industry, London, 1963, no. 29, p 203.

(8) E. Vogel, *Justus Liebigs Ann. Chem.*, **615**, 1 (1958).

(9) G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, **85**, 899 (1964).

(10) G. Lock and K. Stach, *Ber. Deut. Chem. Ges. B*, 77, 293 (1944).

ysis. The nmr spectrum at 100 mhz shows a characteristic A_2B_2 pattern for the cyclobutane protons of **1a**, with 24 observable lines. The trans assignment is probable by comparison with the spectrum of *trans*-1,2-dichloro-1,2-dicyanocyclobutane[11] and the behavior on heating. Exothermic rearrangement occurs when samples of **1a** are heated in bulk to 130–140°. Reproducible first-order decay was obtained on capillary samples, although the ratios of products are somewhat uncertain because of liberation of monomer and HCl. Estimated yields are 24% monomer, 60% **4** (and its decomposition products, **6** and **7**), 12% **5**, and 4% of another isomer identified spectrally as **8**.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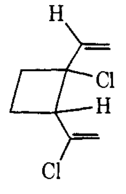

9

The absence of **9**, or its cis isomer, is reasonably certain from the isomeric purity of **5** as isolated. The melting point of the latter precludes any significant amount of 1,5-dichloro-1,5-cyclooctadiene impurity expected by rearrangement of **9**. The absence of **4a** is likewise assured by the absence of 3-chloroethylbenzene, which should be readily detectable if present as an impurity in **7**.

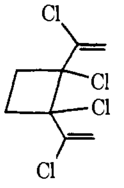
Reaction rates and isomer ratios were observed for temperatures from 25 to 140°.[12] Isomer ratios extrapolated to zero conversion are shown in Table I. Also given are ratios of **2**:**3** found by higher temperature analysis and the yield of **5** obtained under these conditions, which includes pyrolysis yield from **1a** and **1b**. Observed trends are sufficiently consistent that they are probably real, but are sufficiently small that calculated differences in activation energy are near the limits of experimental accuracy. Kinetic parameters for rearrangement of **1a** and **1b** are given in Table II, and dimerization parameters in Table III.

Table I. Isomer Distribution from Chloroprene Dimerization

			Isomer						
T, °C	Time, hr (min)	% Rn	**1a**	**1b**[a]	**4**	**2** + **3**	**5**	**2**/**3**[b]	**5**[b]
25	120	1.8	42	11	14	30	2.4		
25	912	12.3	41	2	10	33	14	51/49	22
60–81[c]	96	64	30	3	18	32	17		
100	(5)	1.25	34	8	20	29	8		
100	(60)	14.6	31	3	20	30	16	38/62	21
140	(2.5)	11	28	3	25	29	15		
140	(10)	30	18	3	26	32	20	35/65	22
25	[0][d]	[0]	41	16	13	30			
65	[0][d]	[0]	36	18	16	30			
100	[0][d]	[0]	33	17	20	30			
140	[0][d]	[0]	28	20	22	30			

[a] Includes small amounts of **6** and perhaps unidentified material. [b] Determined at 200°, **5** includes pyrolysis yield from **1a** and **1b**. [c] Atmospheric reflux. [d] Average values extrapolated to zero reaction.

Under similar conditions, 2,3-dichloro-1,3-butadiene (**10**) yielded three chromatographic products, **11**, **12**, and **13**, in approximately a 1:2:1 ratio. After evaporation of monomer and crystallization of **13**[13] from the mixture, **11** was also obtained in crystalline form, leaving a residue rich in **12**. Structures of these isomers are obvious from comparison of spectra to the corresponding chloroprene products. Spectra of the mixture and crystallization yields are in agreement with the chromatographic composition at moderate conversion. No attempt to resolve the cis isomer of **11** was made in view of the higher temperatures needed for elution. Dimerization rates and the rate of isomerization of **11** (primarily to **12**) are given in Tables II and III.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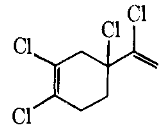
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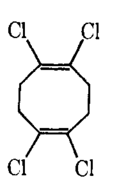
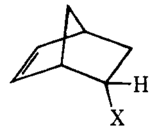

13

The few analyses which have been reported on the products of dimerization of butadiene itself have been obtained under conditions such that only a small amount of divinylcyclobutanes formed would still be present. An available sample of butadiene 10 months old was sampled and found to contain 2.5% total dimers of composition 98.4% vinylcyclohexene, 1.4% *trans*-divinylcyclobutane, 0.2% cyclooctadiene, and less than 0.1% of an impurity which was probably *cis*-divinylcyclobutane. From the reported dimerization rate,[14] 2.6% dimers is predicted at an average temperature of 25°. Products predicted from the thermokinetic scheme of Benson[15] are 37% vinylcyclohexene, 1.8% cyclooctadiene formed directly, and 61% divinylcyclobutane, of which about one-fourth should be cis isomer, largely rearranged to cyclooctadiene under the conditions employed.

To examine the behavior of chloroprene as dienophile with a more conventional diene, codimerization of a mixture with cyclopentadiene was examined. Two new dimer components were observed in a 12:1 ratio. The major component was readily identified as **14a** by comparison of its nmr spectrum with that of known analogs, **14b**, **14c**, and **14d**.[16] The minor isomer was not purified sufficiently for identification, but is almost certainly not 5-chloro-5-vinylnorbornene (**15**) since it failed to react with piperidine. Relative rates were calculated assuming normal second-order reaction.


14a, X = CCl = CH_2
b, X = CN
c, X = $COOCH_3$
d, X = OH

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[11] E. Lustig, *J. Chem. Phys.*, 37, 2725 (1962).

[12] The "4R" products reported in ref 2 apparently include **4** as well as **1a**, **1b**, and **5**, based on comparison of results.

[13] R. E. Foster and R. S. Schreiber, *J. Amer. Chem. Soc.*, 70, 2302 (1948).

[14] G. B. Kistiakowski and W. W. Ransom, *J. Chem. Phys.*, 7, 725 (1939).

[15] S. W. Benson, *ibid.*, 46, 4920 (1967).

[16] J. C. Davis and T. V. van Auken, *J. Amer. Chem. Soc.*, 87, 3900 (1965).

Table II. Thermal Rearrangement of 1,2-Divinylcyclobutanes

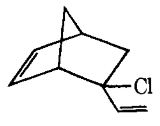
Substituents[a]	Log A, sec^{-1}	E_a, kcal	$k_{373} \times 10^7$, sec^{-1}
(1) Trans Isomers			
None	13.1	34.8	0.5
1,α'-Dimethyl	13.9	34.9	3.2
1,2-Dimethyl	13.9	31.6	250
1,2-Dichloro (**1a**)	14.6	33[b]	200
1,2,α,α'-Tetrachloro (**11**)	(13.9)[c]	(33)[c]	40
(2) Cis Isomers			
None	10.8	23.8	6,300
1,2-Dichloro (**1b**)	11.5	23.8	32,000

[a] Parameters for hydrocarbons are calculated from ref 9. [b] E_a would be 31.8 if log A were 13.9. [c] E_a and rate at 373°K calculated from assumed log A = 13.9.

Table III. Symmetry-Corrected Rate Parameters for Diene Reactions

Diene[a]	Dienophile[a]	Product	Log $A^{b,c}$	E_a^c	Log k_{298}^b	Ref
CPD	TCNE		(4.4)	(3.5)	+1.8	*d*
BD	TCNE		4.4	9.7	−2.7	*d*
2-Cl-BD	TCNE		4.5	13.1	−5.1	*d*
2,3-Cl_2-BD	TCNE		(4.4)	(13.7)	−5.6	*e*
CPD	MA		4.4	8.5	−1.8	*f*
BD	MA		3.6	11.7	−5.0	*f*
2-Cl-BD	MA		4.4	13.6	−5.6	*f*
2,3-Cl_2-BD	MA		4.4)	(15.8)	−7.2	*f*
CPD	CPD		5.5	16.4	−6.5	*g*
CPD	2-Cl-BD	**14a**	(5.5)	(16.9)	−6.9	*h*
2-Cl-BD	2-Cl-BD	(Overall)	6.4, 7.1	20.6, 21.5	−8.7	*i*
			6.7	20.9	−8.6	
		1a	5.7	20.1	−9.0	
		1b	6.3	21.5	−9.5	
		4	6.7	22.1	−9.5	
		2	5.3	20.2	−9.5	
		3	6.3	21.6	−9.5	
2,3-Cl_2-BD	2,3-Cl_2-BD	(Overall)	5.6	20.2	−9.2	
		12	5.7	20.9	−9.6	
		11 + **13**	4.9	19.6	−9.5	
BD	BD	VCH	6.4	23.7	−11	*j*
BD	BD	DVB + COD	(6.4)	(26.0)	−12.7	*k*

[a] Abbreviations: CPD, cyclopentadiene; BD, butadiene; TCNE, tetracyanoethylene; MA, maleic anhydride; VCH, 4-vinylcyclohexene; DVB, 1,2-divinylcyclobutane; COD, 1,5-cyclooctadiene. [b] Rate constants, k_{298}, and preexponential factors, A, are in l./(mol sec) based on product and statistically corrected for symmetry as described in the text. [c] Activation energies in parentheses are calculated from assumed A factors. [d] J. Sauer, private communication. [e] Calculated from chloroprene result given and relative rate from C. A. Stewart, Jr., *J. Org. Chem.*, **28**, 3320 (1963). [f] D. Craig, J. J. Shipman, and R. B. Fowler, *J. Amer. Chem. Soc.*, **83**, 2885 (1961). [g] A. Wassermann, *J. Chem. Soc.*, 1028 (1936). [h] Calculated from dicyclopentadiene rate, cross-dimer relative rate. [i] Calculated from ref 3 of text. [j] Reference 14, text, gas phase reaction. [k] From rate for VCH and product analysis, this work.



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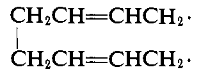
Discussion

From the rates of isomerization of divinylcyclobutanes given in Table II and the products observed in these reactions, a clear dichotomy of mechanism is apparent. As proposed by others,[8,9,15] the cis isomers are believed to undergo a concerted, electrocyclic reaction which is at least formally a Cope rearrangement, forming cyclooctadienes as the only significant products. The trans isomers rearrange much more reluctantly and form a variety of products including monomer, vinylcyclohexenes, cyclooctadienes (perhaps *via* the *cis*-cyclobutanes), racemized starting material,[9] and generally minor amounts of other products. This has been explained on the basis of diradical cleavage by way of the 2,6-octadiene-1,8-diyl diradical, **16**.



$$\begin{array}{l}CH_2CH{=}CHCH_2\cdot\\ |\\ CH_2CH{=}CHCH_2\cdot\end{array}$$

16

Energy relations for the singlet diradical have been discussed by Benson.[15] It is apparent that cis,cis, cis,-trans, and trans,trans forms should exist and that geometric conversion is slow with respect to ring closure or dissociation of the radical. Three position isomers of each form should be possible when the diene units are unsymmetrical in substitution. The triplet state of the same family of diradicals is postulated as an intermediate in the photosensitized dimerization of dienes.[17,18] The triplet is presumed to undergo conversion to the singlet before the ultimate photoproducts are formed. While it is possible that this singlet might differ in energy, conformation, or configuration from the thermally produced diradical, the products observed are generally within the expectations from the proposed energetics.

Although the distinction is not as obvious, it is proposed that a similar dichotomy of mechanism is required for diene dimerizations: one process which leads only to vinylcyclohexenes and requires at least one cisoid diene unit, and a second process which leads primarily to divinylcyclobutanes and permits, but does not require, a cisoid diene unit. Products of the first class include the principal adducts from dimerizations of cyclopentadiene, butadiene, and isoprene,[19] codimeriza-

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(17) G. S. Hammond, N. J. Turro, and R. S. H. Liu, *J. Org. Chem.*, **28**, 3297 (1963); G. S. Hammond, N. J. Turro, and A. Fischer, *J. Amer. Chem. Soc.*, **83**, 4674 (1961); N. J. Turro and G. S. Hammond, *ibid.*, **84**, 2841 (1962); G. S. Hammond and R. S. H. Liu, *ibid.*, **85**, 477 (1963).

(18) W. L. Dilling, *Chem. Rev.*, **69**, 845 (1969).

(19) I. N. Nazarov, A. I. Kuznetsova, and N. V. Kuznetsov, *Zh. Obshch. Khim.*, **25**, 307 (1955).

tion of butadiene with isoprene[20] and of cyclopentadiene with chloroprene (**14a**), and the head-to-tail and tail-to-tail dimers of chloroprene, **2**, and **3**. The process is presumably a conventional Diels–Alder reaction, whether truly concerted or not. Products of the second class include **11** and **13** from dichlorobutadiene, **1a** and **1b** (and **5**) from chloroprene, and the minor amounts of cyclobutane and cyclooctadiene adducts formed where the Diels–Alder process predominates. These products are compatible with a diradical mechanism.

Adducts **4** and **12**, in principle, could arise from either mechanism. Considering that **2** and **3** are formed in comparable amounts, the absence of **4a** suggests that **4** is not formed by the Diels–Alder mechanism. The formation of **14a** but not **15** likewise indicates that the Diels–Alder addition to the chlorine-substituted vinyl group of chloroprene is unfavorable, so that **4** and **12** are presumed to be diradical products for the most part. The additional chlorine atoms on the diradical should increase the difficulty of ring closure particularly for formation of **11** but also for formation of **12**. These steric barriers and competing reversion to monomer provide a natural explanation for the lower ratio of cyclobutanes to cyclohexenes from dichlorobutadiene (50/50) than from head-to-head dimerization of chloroprene (57/13 or 81/19).

Table III lists the kinetic parameters for diene dimerizations and more conventional Diels–Alder reactions of the same dienes. Rates are corrected for symmetry by dividing the experimental result by a factor of 2 for each symmetrical reacting unit. (This is not strictly correct for all possible interpretations of the transition state.) The rates for individual products are calculated from the overall rates and the measured distribution of products. Where no measurement of temperature effects is available, activation energies have been calculated by assuming a preexponential factor. The error introduced is obviously minor in view of the near constancy of this factor over the range of reactions listed.

The activation energy for dimerization of butadiene in cis,trans configuration to vinylcyclohexene is apparently 2.4 kcal more favorable than for trans,trans reaction to divinylcyclobutanes, whereas it should be 1 kcal *less* favorable according to the kinetic scheme of Benson, assuming "free" diradicals. The discrepancy is too large to attribute to the uncertainties of temperature and medium effects or to the assumed stereochemical energy of cisoid *vs.* transoid configurations. There is evidently a stabilization of the order of 3–4 kcal for the cis,trans transition state compared to that expected for a "free" diradical. This could be explained either on the basis of a concerted, electrocyclic transition state or on the basis of a diradical with "secondary interactions"[21] between unbonded termini of the diradical. There are two reasons for preferring the electrocyclic formulation. (1) If secondary interactions in the transition state are as large as indicated, an even greater stabilization is to be expected in the diradical intermediate. This is presumably the same diradical for which Benson has calculated energies based on rearrangement data. It was concluded that this agreed reasonably with expectations for a nonbonded radical. *A priori* calculations for such reactive species are less exact than might be desired, but an error of 5–10 kcal seems unlikely. (2) The thermal formation of **4** and the photochemical production of similar compounds from other dienes should also be susceptible to stabilization by such interactions. No such effect is discernible in the results. It can be argued that stabilization is ineffective because of steric barriers in the case of **4** and energy or conformational barriers in the photo process, but the degree of coincidence required appears unlikely.

Inherent in the arguments given is the assumption that orientation (head *vs.* tail) and configuration of the diene units are determined in the transition state, and that trans,trans intermediates give rise largely to cyclobutanes, cis,trans to cyclohexenes. Other possibilities which may be considered are configurational rotation in an intermediate state, a transition state resembling a charge-transfer association where bonding termini are not yet determined, or a requirement for at least one cisoid diene unit even for cyclobutane formation. These possibilities do not appear attractive, and do not provide any apparent basis for the results obtained, although the evidence against them does not appear conclusive.

It appears most likely, therefore, that both the concerted process and the diradical process for diene dimerizations are possible. Preexponential factors for the two processes are similar, with activation energy favoring the concerted process by several kilocalories except where favorably substituted for diradical reaction, *e.g.*, with chlorine substituents in positions 3 and 6 of the diradical.

Experimental Section

Methods. For gas chromatography, an F & M Scientific Co. Model 720 temperature-programmed instrument was employed with 0.25-in. columns, a helium flow of *ca.* 60 cm^3/min, 150° injection port, and 175° detector temperature to minimize thermal destruction of sensitive compounds. Standard analyses (Figure 1) were obtained with a purchased column described as 2 ft SE-30 silicone gum, 20% on "Diatoport S" support. This column had been used extensively prior to these experiments and subsequent work suggests that a fresh, conditioned column of this composition requires only 1.2–1.5 ft of length for comparable elution temperatures. Normal programming was 70° initially plus 5°/min to 195°. For very low concentrations of diene in monomer, large samples were injected at room temperature, actuating the program after elution of the monomer. Fractionation samples were also examined isothermally as required for elution. Samples were also examined using a 6 ft Carbowax 20M polyethylene glycol column, 5% on Haloport F fluorocarbon support isothermally at 145° or programmed as appropriate, and a 12 ft XF-1150 fluorosilicone oil, 15% on Chromosorb P/AW support used isothermally at 200° to separate **2** and **3** and, incidentally, to obtain pyrolysis of unstable species. The same columns were used for preparative work. Table IV lists retention times for the primary compounds involved for standard conditions on these columns. Quantitative results are based on the assumption that area response per mole of substance (thermal conductivity) is proportional to the square root of molecular weight, except where internal standards were used and calibrated empirically.

Infrared spectra were obtained on neat liquids. Nmr spectra (Varian HA-100) were obtained neat or in deuteriochloroform solution with negligible difference in chemical shift. The distinctive patterns and many sharp peaks in the unsaturation region provided qualitative identifications and integrations of resolvable groups of peaks served for quantitative estimates. Peak frequencies are given in parts per million downfield (negative) from internal tetramethylsilane standard. Fractionations were carried out with a 1-m spinning band column at 2–5 mm pressure. Boiling points as indicated by distillation curves and densities and refractive indices where measured are also given in Table IV.

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[20] R. A. W. Johnstone and P. M. Quan, *J. Chem. Soc.*, 935 (1963).
[21] R. B. Woodward and T. J. Katz, *Tetrahedron*, 5, 70 (1959).

Table IV. Physical Properties of Principal Products[a]

Compd	Bp (~4 mm) or (mp), °C	n^{25}D	Density, 25°	Retention time, min[b] SE-30	Carbowax	XF-1150
7	48	1.5144	1.036	5	2.8	9.6
1a	56	1.5048	1.124	5.9	3.7	
1b				6.7	4.9	
8	58			6.6	3.6	
6	60	(1.512)	(1.103)	6.7	4.9	
4	70	(1.512)		8.4	7.5	
2	72	(1.514)	(1.161)	9.3	7.8	18.0
3	72	(1.514)	(1.161)	9.3	7.8	18.8
5	92	1.5323	1.208	11.7	18.0	38.3
11	(54–60)			13.4		
12				15.6		
13	(93–96)			18.2		
14a	75 (17 mm)			6.2		

[a] Boiling points estimated from fractions. Physical properties in parentheses estimated from mixtures. [b] See text for standard conditions.

Crude Chloroprene Dimerization Mixtures. Redistilled chloroprene was aged under nitrogen at room temperature and at atmospheric reflux in the presence of various inhibitors, usually phenothiazine, picric acid, or the ammonium salt of *N*-nitroso-*N*-phenylhydroxylamine, alone or in combination. No polymer formation was normally observed, but prudence requires that adequate safety precautions be taken to protect against the hazards of uncontrolled polymerization which can occur with monomer of uncertain quality. Chromatographic analyses were performed directly on the monomer–dimer mixture, choosing sample size to obtain a relatively constant quantity of total dimers where possible. Room temperature samples were isolated by low pressure evaporation of monomer at not over 30° and reflux samples were obtained by distilling monomer through a short Vigreux column at 40–60° pot temperature. No qualitative spectral differences were observed. Semiquantitative differences, in agreement with chromatographic results, showed only the decrease in vinyl absorptions (**1b**) and increase in absorptions characteristic of **5**, as expected. These changes were almost independent of temperature if observed at equal monomer conversion. Material balances were obtained by fractionation and analysis of fractions on reaction mixtures from 96 hr atmospheric reflux and were in satisfactory agreement with chromatographic analysis of the whole. No volatile, higher boiling materials were observed. When any polymer was present, it was necessary to treat the residue with hexane to extract **5** from polymer and inhibitor to obtain satisfactory recovery.

Whole dimer samples from room temperature reaction were (1) passed through the chromatograph preparatively, (2) heated briefly to 100°, and (3) allowed to stand at room temperature. Except for conversion of **1b** to **5** and minor dehydrochlorination of **4** to **6** and **7**, no changes could be detected spectrally or chromatographically.

Dimerizations at 100 and 140° were accomplished in sealed capillary tubes to contain monomer and permit rapid heating and quenching. A small amount of polymer was formed at the higher conversion, as indicated by viscosity and internal standard analysis.

A sample of reflux dimer mixture was distilled at atmospheric pressure, to a maximum pot temperature of 250°, reducing the pressure only to strip volatiles at the end of the process. The recovered material, excluding monomer formed in the process, was found to contain 23% **7**, 0.6% **8**, 10% **6**, 42% **2** and **3**, and 25% **5**. Except for the low yield of **8**, this is in reasonable agreement with predictions from the degradation products of the separate isomers.

Characterization of 1,2-Dichloro-1,2-divinylcyclobutane (1a) and 1,6-Dichloro-1,5-cyclooctadiene (5). These components were isolated in adequate purity by refractionation of cuts from material balance distillations of crude dimers. From cooling curves, a melting point of 6–8° was estimated for **5** of 99% purity by gc. Another sample, obtained after extensive thermal decomposition of **1a**, was treated with piperidine to remove allylic halide impurities and redistilled (97% pure), mp 10.5° (lit.[5] mp 13.8°). Nmr absorptions were at 5.76, 2.76, and 2.34 ppm in a ratio 1:2:2 with no apparent splitting. The infrared absorption at 1500 cm^{-1} was useful for discrimination from other isomers and was plainly present in crude dimer mixtures which had not been exposed to heat. A fraction of **1a**, 99% purity, melted at −28 to −26°. The ir spectrum is noted in the text. The nmr spectrum showed a typical vinyl pattern at 6.35–6.05 and 5.45–5.20 and an A_2B_2 multiplet in two groups centered on approximately 2.8 and 2.3 ppm with 12 discernible lines in each half. Piperidine reacted with **1a** much less rapidly than with **4**, but sufficient reaction was obtained at 80° to examine the dimer mixture for nonreactive species that might elute at the same time.

Characterization of 1- and 2-Chloro-4-(1-chlorovinyl)cyclohexenes (2 and 3). Fractionation was ineffective in separating **2**, **3**, and **4**, although **4** was slightly enriched in early samples. Removal of **4** was effected by heating 20 ml of mixed isomers with 15 ml of piperidine for 6 hr on the steam bath, extracting the reaction mass with aqueous HCl, and redistilling to isolate **2** and **3** essentially free of other impurities. Analysis, XF-1150, indicated no change in the ratio of **2** to **3**. The nmr spectrum consisted of a characteristic fringed peak for ring =CH at 5.72, $=CH_2$ at 5.17 and 5.15, and unresolved absorptions at 2.7–1.6 ppm. Irradiation of the allylic region narrowed the 5.72 band to a sharp, apparently single peak. Partial separation by preparative chromatography indicated that the low-field absorptions did indeed overlap, and that the high-field absorptions, while different, were still not resolvable. Sulfuric acid hydrolysis[6] produced only tars in our hands. Heating 15 g of mixed **2** and **3** with 50 ml of dipropylene glycol and 5 g of NaOH for 30 min at 140° produced dehydrochlorination to a new acetylenic species eluting at 4.9 min (silicone). Hydrolysis of the acetylene was accomplished in 53% yield with mercuric sulfate in acetic acid to give a ketone indistinguishable from the chloroprene–methyl vinyl ketone adduct,[22] retention time 9.9 min. Neither the acetylene nor the ketone could be resolved chromatographically or spectrally, and this course was not pursued.

Characterization of 1,4-Dichloro-4-vinylcyclohexene (4). Spectral properties deduced by the removal of **4** from mixture with **2** and **3** were confirmed by a sample later isolated from partial rearrangement of **1a** (see below). Ir showed vinyl absorptions (10.1, 10.8) and the nmr showed vinyl, 6.2–5.9 and 5.4–5.1, ring =CH at 5.78, poorly resolved ring methylenes at 3.0–1.9. Aminolysis apparently resulted in displacement, since no dehydrochlorination products were observed, but the amine resisted attempts at crystallization.

Mixtures of **2**, **3**, and **4** were heated to observe the "thermal" dehydrochlorination of **4**, reaction occurring in some cases as low as 100°. A 20-ml sample containing 42% **4** was heated 10 min at 140°, then 10 min at 170–180°, producing 65% conversion of **4** and comparable amounts of **6**, **7**, and a high-boiling, piperidine reactive product eluting near **5**. The latter decreased on further heating. After concentration by fractionation of several combined samples, **6** and **7** were separated from each other by preparative chromatography. Molecular formulas of C_8H_9Cl were verified by mass spectroscopy. Compound **6** was found to contain one vinyl group, 6.49–6.20 and 5.12–4.93 ppm, two ring =CH groups, 5.85 and 5.66, and four allylic protons, 2.94 ppm. The 1,4-cyclohexadiene structure assigned seems more probable than the fully conjugated alternate in view of the chemical shifts. Compound **7** was identical with an authentic sample[10] by ir, nmr, and chromatography, and lacked bands expected for a meta-disubstituted benzene. Heating a mixture of **6** and **7** at 160° for 10 min produced no change, but after addition of 2% toluenesulfonic acid, 60% isomerization of **6** to **7** was effected in 20 min at the same temperature.

Thermal Rearrangement of Divinylcyclobutanes. When 20 ml of **1a** was heated in a reflux apparatus under nitrogen, a rapid temperature rise occurred from about 130 to 170°, and the temperature soon fell to 120°, with reflux of liberated monomer. Analysis indicated 75% conversion of **1a** with yields of about 22% monomer, 68% **4**, and 10% **5**. Chromatography at 200° on the XF-1150 column gave complete conversion of **1a**, 24% yield of monomer, 13% **5**, and 63% of intermediate material. From larger samples, the intermediates were trapped and analyzed, corresponding to 4% **8** based on **1a**, the balance being **6** and **7**. Distillation of products from several decompositions concentrated **8**, which was then isolated by preparative chromatography. Nmr showed $=CH_2$ at 5.16, ring CHR at 3.32, ring methylenes at 2.06 to 1.96. Ir, as deduced from distillation fractions containing **6** and **7**, showed a strong 11.3 band. No increase in the amounts of **2** and **3** was observed, suggesting that rearrangement of **8** was minor under conditions producing nearly complete decomposition of **1a**. Decomposition rates for **1a** were measured at 100 and 135° in

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(22) A. A. Petrov and N. P. Sopov, *Zh. Obshch. Khim.*, 17, 1295 (1947).

capillary tubes. Rearrangement of **1b** was followed chromatographically during dimerizations, rate constants being calculated from smoothed plots of **1b** and **5** *vs.* dimerization and cross plots of dimerization *vs.* time. A fraction of mixed dimers enriched in **1b** was also isolated by low pressure simple distillation to verify the rate of rearrangement without correction for continued formation.

2,3-Dichlorobutadiene. Redistilled **10** was inhibited and heated in a sealed container for 48 hr (60°) and found to contain 24% dimers, composition 22% **11**, 51% **12**, and 27% **13**. The first two products were found to react with piperidine. Monomer was evaporated and **13** largely crystallized by addition of hexane and cooling, mp 93–96°, after one recrystallization (lit.[1] 98–99°). Distillation of the residue, 79–90° (<2 mm), produced a fraction from which crystals of **11** slowly separated. These were used to seed a lower temperature crystallization to produce **11**, mp 54–60°, and leave a residue containing 78% **12**. The nmr spectrum of **13** showed a single peak at 2.89; for **11**, sharp $=CH_2$ peaks at 5.76 and 5.61, and broad methylene multiplets centered at 3.05 and 2.38; for **12**, $=CH_2$ at 5.62, 5.48, methylenes at 3.09, 2.60, and 2.34. Spectral and material balance calculations confirmed the chromatographic composition. Dimerization rates were also measured at room temperature as for chloroprene. Decomposition of **11** was measured at 160°, using the crude distillation mixture, which precluded accurate measurement of products.

Butadiene. From a dip-leg cylinder of commercial CP butadiene 10 months old from the date of filling, liquid butadiene was removed into a cooled flask. Trichlorotrifluoroethane containing a small amount of tetrachlorobutane internal standard was added, butadiene removed under reflux, and the resulting solution chromatographed with 30° initial column temperature. Vinylcyclohexene and cyclooctadiene peaks were verified by comparison to known samples and by mass spectroscopy, *trans*-divinylcyclobutane only by mass spectroscopy. A small peak which was probably the cis isomer was too small for positive identification

Cross-Dimerization of Chloroprene and Cyclopentadiene. An inhibited solution of 3.9 g of freshly distilled cyclopentadiene and 14.5 g of chloroprene was aged at room temperature and intermittently analyzed over 300 hr time. New peaks were observed at 6.2 and 8.2 min retention time with relative rates of formation calculated to be 0.20 and 0.013 relative to dicyclopentadiene assuming that the compounds were cross dimers. A relative rate for chloroprene was estimated at 0.0024 compared to 0.0016 calculated from Table III. For preparative purposes, a mixture of 96 g of chloroprene and an equal weight of partially dimerized cyclopentadiene was refluxed for 2 hr at 45–55°, allowed to stand overnight, and distilled. Analysis indicated 60 g of dicyclopentadiene, 12 g of **14a**, 1.1 g of the unidentified material, and negligible amounts of chloroprene dimers. Redistillation provided **14a**, 74–76° (17 mm), nmr $=CH$ at 6.12, 5.88, $=CH_2$ at 5.04, 4.87, bridgehead CH at 3.14, 2.85, exo protons at 2.95, 1.90, bridge protons at 1.42, 1.25, and the endo proton at 1.02. Splitting patterns were very similar to **14c**.[14] The small amount of remaining cross dimer was not isolated from the residue, but was found to remain unchanged when heated with piperidine.

The Use of Added Sodium Azide as a Mechanistic Probe for Solvolysis Reactions

Douglas J. Raber,[1a] J. Milton Harris,[1b] Robert E. Hall,[1c] and Paul v. R. Schleyer*

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540.
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Abstract: The solvolysis of 2-propyl tosylate, 2-adamantyl tosylate, and 1-adamantyl bromide in 80% ethanol and 75% dioxane in the presence of sodium azide has been investigated in order to gain information on the role of solvent in solvolytic reactions of secondary substrates. Failure to observe a rate–product correlation for 2-adamantyl tosylate and 1-adamantyl bromide indicates nonidentity of the rate-determining and product-determining steps and the absence of nucleophilic solvent participation. However, the observed rate–product correlations for the solvolysis of simple, unhindered secondary derivatives (2-propyl tosylate, 2-octyl brosylate) are consistent with nucleophilic solvent participation in the solvolysis of these compounds. The ion pair hypothesis of Sneen is analyzed, and it is concluded that his data do not demand the intermediacy of ion pairs in the solvolysis of 2-octyl derivatives. The stability–selectivity relationship for carbonium ion reactions in the presence of azide ion has been extended to considerably less reactive substrates. The available evidence demonstrates the limiting nature of 2-adamantyl solvolysis.

The technique of adding strong nucleophile (*e.g.*, lyate ion or azide ion) to a solvolysis medium as introduced by Hughes and Ingold[2] affords a direct measure of the tendency of a substrate to react by a unimolecular or bimolecular pathway. The characterization of a reaction as unimolecular (SN1) or bimolecular (SN2) has been of fundamental importance in the study of the mechanism of solvolysis. The molecularity of the reaction with solvent cannot be determined, but inferences may be made from the kinetic order of the reaction with added nucleophile.[3]

When an added nucleophile produces a marked rate enhancement, a bimolecular displacement process is indicated. The use of sodium azide permits additional information to be derived from product composition; the product of attack by lyate ion is indistinguishable from the normal solvolysis product, but attack by azide ion leads in contrast to an isolable alkyl azide. The combination of kinetic and product data permits the

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(1) (a) National Institutes of Health Postdoctoral Fellow, 1968–1970; (b) National Institutes of Health Postdoctoral Fellow, 1969–1970; (c) A. B. Thesis, Princeton University, 1970.

(2) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1969; (b) L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

(3) Ingold and his coworkers discussed several approaches to this problem.[2] These are: studies of mass law effects, salt effects, and variations in structure, nucleophile, and solvent. One of the most powerful tools was shown to be the use of added azide ion.