bomb (50 ml in volume) supplied by the Parr Instrument Co. The apparatus was flushed several times with oxygen, and oxygen was then introduced into the bomb at the desired pressure, making a rough allowance for the increase in pressure on raising the temperature. The bomb was then heated, without agitation, to 60 or 70° by means of a custom-made heating mantle for the desired length of time, measuring the temperature (±5°) by a thermocouple. The pressure fluctuated somewhat (±5–15%), especially at the higher pressures, and values reported are "averages." The bomb was then allowed to cool to room temperature before slowly releasing the oxygen. Because of possible explosions, strict safety precautions (special explosion-proof rooms, remote control of the bomb at all times, etc.) and proper equipment are mandatory.

The products from decompositions using Freon TF were reduced by hydrogenation. In a typical reduction, the solution from the decomposition was transferred, along with ether or Freon TF washings, from the bomb to the glass bottle of a Parr hydrogenator. Catalyst, 0.50 g of 10% palladium on charcoal, was added, and hydrogenation carried out for about 1.5 hr at ambient temperature and an initial hydrogen pressure of approximately 50 psi. The catalyst was removed by filtration, and the solution concentrated by distillation at atmospheric pressure through a 4–4.5-cm column (packed length) filled with perforated stainless steel plates, followed by pumping down twice to *ca.* 180 mm on a rotary evaporator. Concentration was necessary since the solvent interfered with glpc analysis on the standard 0.25-in.-diameter columns when large samples (necessitated by the dilute nature of the solution) were injected. Products were not fractionated by this concentration procedure as shown by the consistency of the results in various runs.

Solutions were analyzed by glpc using Varian–Aerograph A-90-P and Perkin-Elmer Model 226 gas chromatographs. Products were identified by peak enhancement on addition of authentic compounds. Yields were obtained by comparison of peak areas with those obtained from standard samples. Separation of *exo* and *endo* alcohols **4** was by use of a 150 ft × 0.01 in. (i.d.) Quadrol capillary column. Other separations were accomplished by various standard columns.[19]

Registry No.—1,4-Dimethylcyclohexyl radical, 24151-68-6; 2-methylnorbornyl radical, 24212-34-8; *trans*-1,4-dimethylcyclohexanecarboxylic acid, 24097-70-9; *cis*-1,4-dimethylcyclohexanecarboxylic acid, 24097-71-0; *trans*-1,4-dimethylcyclohexanecarbonyl chloride, 24097-72-1; *cis*-1,4-dimethylcyclohexanecarbonyl chloride, 24097-73-2; *cis*-**1**, 24097-65-2; *trans*-**1**, 24097-66-3; *cis*-**1**-CO_2CH_3, 23250-42-2; *trans*-**1**-CO_2CH_3, 23059-38-3; *exo*-**3**, 24162-40-1; *endo*-**3**, 24097-69-6.

Acknowledgment.—We thank Professor H. C. Brown and Dr. M.-H. Rei for information concerning separation of 2-methylnorbornanols. We gratefully acknowledge a National Research Council Fellowship for W. G. S. and an Alfred P. Sloan Foundation Fellowship for R. E. P.

Kinetics of the Reverse Diels–Alder Dissociation of Substituted Dicyclopentadienes

WILLIAM E. FRANKLIN

Southern Regional Research Laboratory,[1] New Orleans, Louisiana 70119

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The kinetics of the dissociation of dicyclopentadienes substituted with alkyl and ester groups were measured. The effects of these groups on the kinetics of the dissociation are described. The dimer of *t*-butylcyclopentadiene was prepared and found to be 1,4-di-*t*-butyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene.

Although kinetics of the dissociation of dicyclopentadiene have been the subject of a number of studies,[2] there is very little information in the literature on the dissociations of substituted dicyclopentadienes. In a previous communication from this laboratory,[3] the kinetics of the dissociation of dicyclopentadiene (**1**) and the methyl esters of dicyclopentadienemonocarboxylic acid (4-carbomethoxytricyclo[5.2.1.0^{2,6}]-deca-3,8-diene, **2**) and dicyclopentadienedicarboxylic acid (4,9-dicarbomethoxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene, **3**) were reported.

Reactive dienophile trapping agents removed the monomer as it was formed and allowed measurement of the dissociation reaction without interference from the dimerization reaction. These dissociations followed first-order kinetics with respect to the dimer[4] and were independent of the nature or concentration of the trapping agent.[3]

The previous kinetic measurements had been made by a novel and rapid technique using a differential scanning calorimeter,[3] and this technique was extended to other substituted cyclopentadiene dimers which were available. This communication reports the results of these measurements.

Results

The kinetics of the dissociation reactions were measured with the differential scanning calorimeter, which measures directly the rate of absorption or evolution of heat in the sample as its temperature is being raised at a controlled rate. Liquid samples, such as the solution samples used in the present work, are in a layer of 1 mm or less thickness and are in good thermal contact with the heating and temperature sensing elements of the instrument. Problems of thermal gradients within the samples are therefore largely eliminated in these measurements.

Since the samples are in the form of solutions of reagents, such as are used in more conventional kinetic measurements, the recent criticisms[5] of the use of thermoanalytical methods to obtain kinetic data do not apply to the present measurements.

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] A. Wasserman, "Diels–Alder Reactions," American Elsevier Publishing Co., New York, N. Y., 1965, pp 61–63.

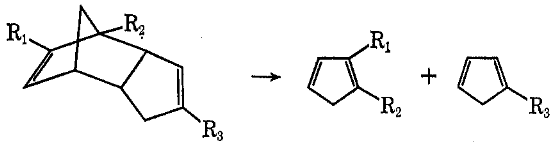
[3] W. E. Franklin, C. H. Mack, and S. P. Rowland, in "Analytical Calorimetry," R. S. Porter and J. F. Johnson, Ed., Plenum Press, New York, N. Y., 1968, pp 181–188.

[4] W. E. Franklin, C. H. Mack, and S. P. Rowland, *J. Org. Chem.*, **33**, 626 (1968).

[5] T. A. Clarke and J. M. Thomas, *Nature*, **219**, 1149 (1968); J. M. Thomas and T. A. Clarke, *J. Chem. Soc., A*, 457 (1968); T. A. Clarke, E. L. Evans, K. G. Robins, and J. M. Thomas, *Chem. Commun.*, 266 (1969).

TABLE I

DISSOCIATION OF DICYCLOPENTADIENES

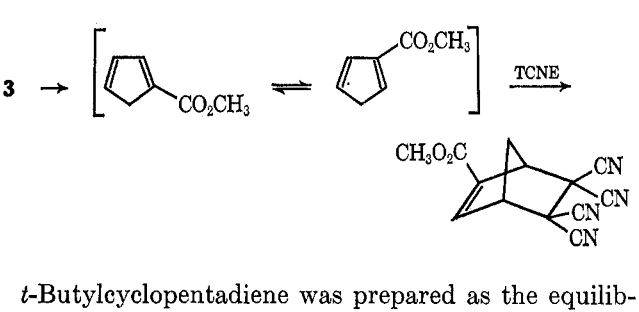


Compound	R$_1$	R$_2$	R$_3$	Trapping agent[a]	E_a, kcal/mol	Log A	ΔS^*, gibbs/mol
1	H	H	H	A	35.1	13.7	1.1
2	H	H	CO$_2$CH$_3$	A	32.2	13.5	0.7
3	CO$_2$CH$_3$	H	CO$_2$CH$_3$	A	30.5	13.1	1.5
				B	30.0	13.3	0.5
				C	30.8	13.1	1.4
4	CO$_2$C$_6$H$_5$	H	CO$_2$C$_6$H$_5$	C	29.4	12.8	2.9
5	CH$_3$, H		CH$_3$	C	37.1	14.4	4.3
6	H	t-C$_4$H$_9$	t-C$_4$H$_9$	B	27.0	12.5	−3.9
				D	27.2	12.7	−3.1

[a] Trapping agents: A, N-phenylmaleimide in tetraglyme; B, tetracyanoethylene in tetraglyme; C, dibutyl maleate, no solvent; D, evaporation of monomer from open capsule.

The results of the kinetic measurements of the reverse Diels–Alder dissociation of the substituted dicyclopentadienes are given in Table I. The Arrhenius parameters are averages from five or more independent runs for each reaction. The standard deviations were 3% or less of the values for the parameters.

The kinetic parameters found for the dissociation of dicyclopentadiene 1 are quite close to those reported by Khambata and Wasserman[6] for the dissociation of dicyclopentadiene as the pure liquid, E_a = 35.3 kcal/mol, log A = 13.6. The dissociation of the dimethyl ester of dicyclopentadienedicarboxylic acid 3 was measured in the presence of three dienophilic trapping agents. The Arrhenius parameters for these reactions were identical within experimental error, thus indicating that the dissociation of the dicyclopentadiene derivative is the rate-determining step and that the rate of the reaction is independent of the trapping agent. The dissociation is followed by the rapid interconversion between 1- and 2-carbomethoxycyclopentadiene and the reaction of one or both of these isomers with the trapping agent.[4]



t-Butylcyclopentadiene was prepared as the equilibrium mixture of the 1 and 2 isomers to provide a cyclopentadiene holding a bulky substituent group which should decrease the stability of the dimer. The t-butylcyclopentadiene showed no evidence of dimerization by gas chromatography after long standing at 0°, but dimerized fairly rapidly at 120°. The nmr spectrum of the dimer showed two vinyl protons as a doublet at τ 4.15 and one vinyl proton as a characteristic "quartet" at τ 4.10. These features had been found earlier[4] to be typical of 1,4 substitution in the dicyclopentadiene ring system. By analogy with the "liquid dimer" from methyl cyclopentadienecarboxylate,[4] the dimer of t-butylcyclopentadiene is therefore assigned the structure of *endo*-1,4-di-t-butyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene (6). The evidence does not exclude the possibility of the 4,7-di-t-butyl isomer.

The dimethyldicyclopentadiene was the commercially available "methyl cyclopentadiene dimer." The nmr spectrum of this dimer showed a ratio of vinyl to aliphatic protons of 1:5.8, which corresponds to an approximately equimolar mixture of 1,4- and 4,9-dimethyltricyclo[5.2.1.0^{2,6}]deca-3,8-dienes (5). Gas chromatography showed also that the dimer was a mixture of two compounds in approximately equal amounts. A similar mixture of dicyclopentadienedicarboxylic acids was previously found[4] from the low-temperature carbonation of cyclopentadienyl sodium.

The data in Table I show the effects of the type of substitution on the rates of dissociation of the substituted dicyclopentadienes. The entropies of activation are quite close to zero, as has been found in other reverse Diels–Alder reactions.[2]

The energies of activation show both electronic and steric effects of the substituents on the reactions. The first three reactions show the effects of successive substitutions with electron-attracting carbomethoxy groups, where each group decreases the energy of activation by about 2.5 kcal. When the methoxy groups are changed to phenoxy groups, a further slight decrease in activation energy occurs, probably as a result of increased strain on the dicyclopentadiene ring system from the proximity of the two large phenyl groups.

The large activation energy for the dissociation of methyl cyclopentadiene dimer would seem to indicate that the electron-releasing methyl groups tend to hinder the dissociation of the dicyclopentadiene ring system. Although this dimer is a mixture of at least two isomers, the Arrhenius plots for the dissociation were linear over the 40° temperature range of the plots. If there had been substantial differences between the rates of dissociation of the isomers, the

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(6) B. S. Khambata and A. Wasserman, *J. Chem. Soc.*, 375 (1939). More recent values are given in W. C. Herndon, C. R. Grayson, and J. M. Manion, *J. Org. Chem.*, **32**, 526 (1967). These values, however, refer to the dissociation of dicyclopentadiene in the gas phase and correspond to the lower values for the gas phase dissociation given by Khambata and Wasserman.

Arrhenius plots would not have been linear at each of the scan rates used for the measurements.

The kinetic parameters for the dissociation are calculated from the rate of evolution of heat as the reaction proceeds. The quantity of heat evolved by the reaction is the sum of the heats from the slow, endothermic dissociation of the dimer and the fast, exothermic reaction of the monomer with the trapping agent. When the dimer of *t*-butylcyclopentadiene was heated in the presence of N-phenylmaleimide or dibutyl maleate, the heats of the endothermic and exothermic steps were nearly equal. Thus, the heats of the reactions were too small to provide the bases for kinetic measurements. When tetracyanoethylene was used as the trapping agent, as illustrated above in the equation with compound **3**, a small, but measurable, heat of reaction was observed. This was used to calculate the kinetics of the dissociation of the dimer of *t*-butylcyclopentadiene. These kinetic parameters were confirmed by measuring the rate of evaporation as the dimer dissociated to the volatile monomer in open sample capsules in the differential scanning calorimeter.

It was originally assumed that the large *t*-butyl groups would interfere with each other and facilitate the dissociation of the dimer of *t*-butylcyclopentadiene. It was found, however, that the only major product of the dimerization of *t*-butylcyclopentadiene was the 1,4-di-*t*-butyl isomer **6** (see above), in contrast to the dimerization of methyl cyclopentadienecarboxylate, where the 4,9-dicarbomethoxy isomer is the major product.[7] Molecular models of the dimer show that the *t*-butyl groups are well separated from each other, and would not be expected to facilitate the dissociation. By analogy with the dissociation of methylcyclopentadiene dimer, it would seem that the electron-releasing *t*-butyl groups would retard the dissociation of the dimer. It was found, however, that the energy of activation of this dissociation is the lowest value in Table I. There is no readily obvious way to reconcile the low energy of activation for the dissociation of the dimer of *t*-butylcyclopentadiene with the spectral evidence for its structure.

Experimental Section

Sources of Reagents.—Dicyclopentadiene (practical grade, 95%), tetracyanoethylene, and N-phenylmaleimide were recrystallized to constant melting point before use. Reagent grade dibutyl maleate was used without further purification. Tetraglyme was purified by vacuum distillation from calcium hydride [bp 105° (0.5 mm)]. The preparations of 4-carbomethoxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene, 4,9-dicarbomethoxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene, and 4,9-dicarbophenoxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene have been described previously.[4] Methylcyclopentadiene dimer was used as obtained from Aldrich Chemical Co.[8]

t-Butylcyclopentadiene was prepared as the equilibrium mixture of the 1 and 2 isomers from cyclopentadienyl sodium and *t*-butyl bromide by the method of Riemschneider.[9] The dimer of *t*-butylcyclopentadiene was prepared by heating the monomer at 120° for 7 hr under a stream of nitrogen, and then removing the small amount of unreacted monomer *in vacuo*. The solid dimer was recrystallized from methanol to give 1,4-di-*t*-butyltricyclo[5.2.1.0^{2,6}]deca-3,8-diene (**6**): mp 65-66° (lit.[10] mp 69°); nmr τ 4.1 (d, 2 H), 4.9 ("quartet," 1 H), 9.1-9.2 (2 s, 18 H).

Kinetic Measurements.—All kinetic measurements were made with the Perkin-Elmer DSC-1 differential scanning calorimeter.[8] The measurements were made on 10-20-μl samples of solutions of the dimer, trapping agent, and solvent or excess liquid trapping agent contained in sealed aluminum capsules. The technique and calculations of the kinetic parameters have been described previously.[3] The calculations were carried out on a Control Data Corp. 1700 digital computer. The Arrhenius parameters were calculated from rate constants over 40-80° ranges between 390° and 525°K, depending on the scan rates and the values of the kinetic parameters. Each set of kinetic parameters recorded is the average from five or more independent runs at two or more scan rates. The standard deviations for the kinetic parameters were 3.5% of the values or less.

Registry No.—**1**, 77-73-6; **2**, 22388-06-3; **3**, 23163-00-0; **4**, 24164-80-5; **5**, 7570-08-3; **6**, 24165-37-5.

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(7) D. Peters, *J. Chem. Soc.*, 1042 (1961).

(8) Mention of a company and/or product by the U. S. Department of Agriculture does not imply approval or recommendation of the company or product to the exclusion of others which may also be suitable.

(9) R. Riemschneider, A. Reisch, and H. Horak, *Monatsh. Chem.*, **91**, 805 (1959).

(10) R. Riemschneider and R. Nehring, *ibid.*, **90**, 568 (1959).