Cyclopropanes. XXVIII. The Rearrangement and Reactivity of the 1-Methyl-2,2-diphenylcyclopropyl Radical[1]

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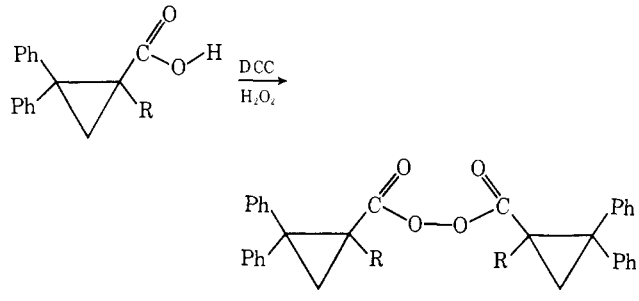
Abstract: It was observed that, in solution, the 1-methyl-2,2-diphenylcyclopropyl radical (**9**) either reacts with hydrogen atom donating solvents to yield 1-methyl-2,2-diphenylcyclopropane (**5**) or rearranges to the 3,3-diphenyl-2-methylpropenyl radical which subsequently dimerizes to 1,1,6,6-tetraphenyl-2,5-dimethyl-1,5-hexadiene (**6**). By determining the ratio of **5**:**6** one is able to evaluate the relative ability of various solvents to donate hydrogen atoms to the cyclopropyl radical. Evidence is provided to show that 1-methyl-2,2-diphenylcyclopropyl radical is less selective (more reactive) than a chlorine atom.

In our studies concerned with the reaction of metals such as lithium,[2] sodium,[3] and magnesium[4] with 1-halo-1-methyl-2,2-diphenylcyclopropane it was postulated that the 1-methyl-2,2-diphenylcyclopropyl radical was involved as an intermediate. Moreover, some results[4] in the Grignard formation reaction suggested that this radical abstracted a hydrogen atom from diethyl ether at a faster rate than from tetrahydrofuran. The relative reactivity indicated for these two solvents seemed questionable. If one considers the cyclic structure of tetrahydrofuran, the radical abstraction of a hydrogen atom from the 2 position would lead to a decrease in the 1,2-hydrogen nonbonded interactions. Due to the flexible chain structure of diethyl ether this relief of steric strain would not be obtained and on this basis one might conjecture that tetrahydrofuran would be a better hydrogen atom donor than diethyl ether toward radicals. In order to ascertain the nature of the 1-methyl-2,2-diphenylcyclopropyl radical (**9**) this ancillary study was undertaken and designed to generate the desired cyclopropyl radical in an unambiguous manner and to evaluate solvent reactivity toward it.

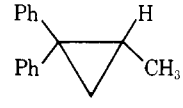
Results and Discussion

Synthesis and Product Study. The reliability of diacyl peroxides as a source of alkyl radicals has been thoroughly established[5] and they were therefore selected as precursors for the desired cyclopropyl radicals. 2,2-Diphenylcyclopropanecarbonyl peroxide (**1**), 1-methyl-2,2-diphenylcyclopropanecarbonyl peroxide (**2**), and 1-bromo-2,2-diphenylcyclopropanecarbonyl peroxide (**3**) were prepared by the convenient method described by Greene and Kazan.[6] The peroxides **1** and **2** were crystalline and remarkably stable; they could be stored in the pure state at room temperature for several months without appreciable decomposition. However, peroxide **3** was less stable and could only be stored, under refrigeration, for several weeks.



1, R = H
2, R = CH_3
3, R = Br

The thermal decomposition products of **2** in a number of solvents were examined in some detail. Decomposition of **2** in benzene produced 1-methyl-2,2-diphenylcyclopropanecarboxylic acid (**4**), 1-methyl-2,2-diphenylcyclopropane (**5**), 1,1,6,6-tetraphenyl-2,5-dimethyl-1,5-hexadiene (**6**), and 2-methyl-4,4-diphenyl-Δ^2-γ-butyrolactone (**7**). The structure of lactone **7**



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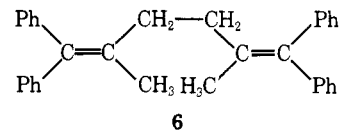

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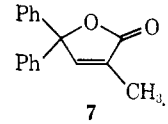

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was established by spectral data and independent synthesis (see Experimental Section).

Assuming the acyloxy radical **8** is produced from the decomposition of the diacyl peroxide **2** it could react in benzene in a number of ways: by abstraction of a proton from a suitable source to yield the carboxylic acid **4**, by decarboxylation to yield the cyclopropyl radical **9**, or by an intramolecular radical attack on the cyclopropyl ring to yield the tertiary radical **10** which by loss of a hydrogen atom produces the lactone **7**.

The total reaction products isolated (**4**–**7**) from the decomposition of **2** in benzene were about 65% with

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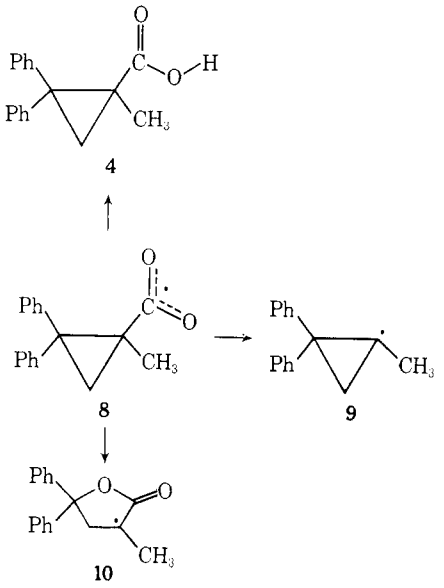
(2) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3283 (1964); H. M. Walborsky and M. S. Aronoff, *J. Organometal. Chem.*, **4**, 418 (1965).

(3) J. B. Pierce and H. M. Walborsky, *J. Org. Chem.*, **33**, 1962 (1968).

(4) H. M. Walborsky and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3288 (1964).

(5) D. F. DeTar and D. V. Wells, *ibid.*, **82**, 5839 (1969), and references cited therein.

(6) F. D. Greene and J. Kazan, *J. Org. Chem.*, **28**, 2168 (1963).

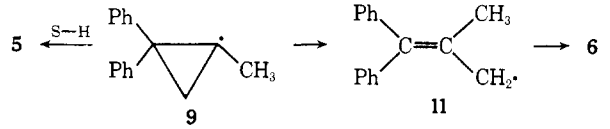


lactone **7** comprising 40% of the mixture. Attempted separation of the remaining tarry product by various types of chromatography failed. No 1,1-dimethyl-2,2-diphenylethylene or dimeric dicyclopropyl compounds from the decomposition of **2** was detected by vpc analysis. Neither was 1,1-dimethyl-2,2-diphenylethylene detected even when the decomposition was carried out in methanol as a solvent.

The failure to detect coupling product from radical **9** or from the unsubstituted cyclopropyl radical[7] is not too surprising. The ratio of combination to disproportionation product of a number of radicals has been studied and the results compiled by Pryor.[8] The data indicate that disproportionation becomes more important the more branched the radical. Consequently, even when two tertiary radicals, **9**, react in a solvent cage[9] they disproportionate rather than dimerize.

Reaction of 1-Methyl-2,2-diphenylcyclopropyl Radical (9). Whether **9** was derived from the acyloxy radical **8** or directly from **2** by a concerted process (cleavage of the O–O bond simultaneously with loss of CO_2) could not be determined at this point. However, this was not important to the present studies, although the isolation of **4** and **7** can be taken as evidence for **8** as the intermediate.

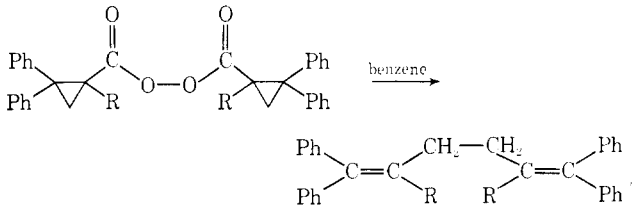
Based on the products observed from the decomposition of **2** the reaction of **9** can be rationalized largely in terms of the following reaction scheme: abstraction of a hydrogen from solvent (SH) to give **5**; isomerization to the allylic radical **11** followed by dimerization to give **6**. The abstraction of hydrogen



from solvent by the allylic radical to give 1,1-diphenyl-2,2-dimethylethylene did not occur. This is consistent with the result reported by McNesby and Gordon[10] who have observed that allyl radicals disappear *via* radical–radical combination until 450° and hydrogen abstraction does not occur below this temperature. These authors have rationalized this in terms of the great stability of the allyl radical. In the present system, substitution of phenyl rings in the 3 position of the allylic radical leads to a larger resonance stabilization than in simple allylic radicals; therefore it is not surprising to find that the 2-methyl-3,3-diphenylallyl radical does not abstract hydrogen appreciably under the reaction conditions of the decomposition of the peroxide (64–65°).

Formation of **6** is noteworthy since it is believed to represent the first observed case of the isomerization in solution of a cyclopropyl radical to an allyl radical.[11] Similar isomerization products were also observed from **1** and **3**. In the case of **1**, a secondary radical would be generated while **2** and **3** would generate a tertiary radical at one of the ring atoms. Apparently the substitution of two phenyl rings[12] in the 2 position markedly lowers the energy barrier to isomerization as well as leading to a more stabilized allylic system **11**. Table I gives the yields of the isomerization products from **1**, **2**, and **3** in benzene.

Table I. Isomerization Products of the Cyclopropyl Radical



Peroxide, R	Temp, °C	Product, R	% yield
H	80	H	34
CH_3	64–65	CH_3	24
Br	80	Br	25

The isomerization of the 1-methyl-2,2-diphenylcyclopropyl radical (**9**) can be prevented by the presence of a good radical trapping reagent as shown in Table II. The isomerization product **6** was observed in runs 1–14 but no such product was observed in runs 15–19. This demonstrates that **9** reacts with thiophenol, chloroform, carbon tetrachloride, and iodine faster than it isomerizes to the allyl radical **11**.

The values given in the second and third column in Table II are the results of the quantitative analyses of **6** and **5** based on the vpc internal standard method. The values given in the fourth column are the yields of crude acid **4**. The yield of **4** seems to be higher in the case of alcoholic solvents (runs 3, 8, 13, and 14). Besides the products listed in Table II, a large amount of phenyl disulfide was isolated from the thiophenol reaction (run 15). In run 18, a 19–23% yield of 1-iodo-1-methyl-2,2-diphenylcyclopropane was obtained and

(7) H. Hart and D. P. Wyman, *J. Amer. Chem. Soc.*, **81**, 4891 (1959).
(8) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.
(9) H. M. Walborsky and J.-C. Chen, *J. Amer. Chem. Soc.*, in press; *ibid.*, **89**, 5499 (1967).
(10) J. R. McNesby and A. S. Gordon, *ibid.*, **79**, 825 (1957).
(11) A preliminary report was published: H. M. Walborsky, J. C. Chen, and J. L. Webb, *Tetrahedron Lett.*, 3551 (1964).
(12) The decomposition of the diacyl peroxide of *trans*-2-phenylcyclopropanecarboxylic acid did not give rise to rearranged product (private communication from C. J. Chen). Apparently two phenyl rings or their equivalent is necessary.

Table II. Decomposition of 2 in Various Solvents

Run no.	Solvents	Products, % 6	5	4	Relative reactivity (per active hydrogen)
1	Benzene	11.95	5.85	4	0.23
		8.60	3.52	3	
		9.22	3.76	3	
2	Cyclohexane	7.14	3.98	9	0.30
		7.32	4.48	6	
		7.38	4.06	4	
3	*tert*-Butyl alcohol	2.71	2.70	19	0.33
		3.11	2.78	19	
4	Acetone	6.77	6.77	7	0.51
		6.85	6.73	5	
5	Diethyl ether	9.61	7.37	2	0.57
		11.40	7.84	2	
6	Ethyl acetate	7.50	4.52	2	0.92
		8.34	4.84	5	
7	Toluene	8.34	7.41	5	1.00
		6.23	6.35	4	
8	Methanol	1.27	1.49	42	1.24
		1.55	1.89	41	
9	Tetrahydrofuran	6.45	6.98	2	1.44
		6.55	7.21	2	
10	Acetonitrile	4.62	8.35	12	1.76
		3.56	5.69	12	
11	Ethylbenzene	3.82	4.32	4	1.77
		3.72	4.20	5	
12	Cumene	1.77	1.45	3	2.50
		2.83	2.18	3	
13	Ethanol	1.53	3.00	44	3.05
		2.16	4.21	45	
14	Isopropyl alcohol	2.71	4.08	24	4.40
		2.59	3.43	26	
15	Thiophenol	0	10.73	4	
16	Chloroform	0	9.24	7	
		0	9.16	6	
17	Carbon tetrachloride	0	2.06	3	
		0	2.20	3	
18	Carbon tetrachloride and iodine	0	3.71	7	
19	Benzene and iodine	0	3.91	7	

none of the corresponding chloride was able to be detected by vpc analysis showing that iodine, as expected, is more reactive than carbon tetrachloride toward the cyclopropyl radical **9**.

As can be seen from Table II, the yield of products derived from **9** is not very high. The total yield of **5** and **6** is only 5–15% in the nonhalogenated solvents. This is not unexpected since the decarboxylation of the initially formed cyclopropanecarboxy radical is not a favored process and yields the lactone **7** as the main product.

However, a rather high yield of 1-methyl-2,2-diphenylcyclopropyl halides was observed when **2** was decomposed in halogenated solvents or in the presence of iodine: a 20% yield of 1-chloro-1-methyl-2,2-diphenylcyclopropane was observed when the peroxide was decomposed in carbon tetrachloride (run 17), a 19–23% yield of 1-iodo-1-methyl-2,2-diphenylcyclopropane was obtained when the peroxide was decomposed in the presence of iodine (runs 18 and 19). If the cyclopropyl halides were derived only from the halogen abstraction by **9**, a halide yield of more than 15% would not be expected. Apparently, the reaction involved the formation of an intermediate acyl hypohalite which decomposed to the corresponding cyclopropyl halide.

Kochi and Mocadlo[13] have demonstrated that chromious ion-catalyzed decomposition of diacyl peroxides in aqueous alcohol gave a high yield of alkanes. However, the decomposition of **2** in ethanol in the presence of chromous sulfate gave **5** in a 3.5% yield. Thus, the yield was not improved in the presence of chromium ion. This is consistent with our findings and the result recently observed by Kochi and Bemis[14] who reported that the cyclopropanoyl peroxide underwent metal ion catalyzed decarboxylation much more sluggishly than other alkyl diacyl peroxides.

Solvent Reactivity toward 9. In the free-radical hydrogen abstraction reaction there is a possible extraneous source of **5** by the reaction of **9** with a hydrogen donor (R–H) other than the solvent (S–H). Possible sources might be the peroxide itself or its decomposition products. The effect would be to complicate the evaluation of the relative solvent reactivities. In order to test the possibility of such a reaction, **2** was decomposed in benzene-d_6. It was found that no appreciable amount of nondeuterated cyclopropyl compound **5** could be detected by mass spectral analysis. Thus, this reaction as well as the solvent cage disproportionation reaction,[9] such as in the decomposition of the peroxide **2** in carbon tetrachloride **9**, are not important in benzene. As will be discussed later, benzene is the poorest radical trapping reagent among the solvents listed in Table II. It is reasonable to assume that the hydrogen abstraction of **9** from a source other than the solvent (except for the cage reaction, if any) is not important in runs 2–14, Table II. If the cage reaction is not important in runs 2–14, Table II, as in the case of benzene, then the evaluations of the reactivity of solvents are simplified by comparison of the rates of hydrogen abstraction from the solvent with the rate of rearrangement of the radical. Before evaluating the relative solvent reactivities, it has to be assumed that the rate of rearrangement of the cyclopropyl radical to the allylic radical is independent of solvent effects. This assumption is not unreasonable, since radicals are electrically neutral and one might expect that they will not be subject to the same kinds of polar influences that affect the reactions of ions. In this view, radical rearrangement would show little or no solvent effects. An example of insensitivity to polar influences in radical reactions is provided by the fact that relative rates of hydrogen abstraction by methyl radicals are the same in the gas phase as in solution.[8]

Thus, the relative solvent reactivities per hydrogen atom which was defined by Trotman-Dickenson and Steacie[15] (expressed in terms of the reactivity of toluene as 1) can be obtained by the following equation.

$$\text{relative reactivity of a hydrogen donor toward } \mathbf{9} = \frac{\left[\dfrac{\text{(yield of } \mathbf{5} \text{ in SH)}}{2\text{(yield of } \mathbf{6} \text{ in SH)(no. of active hydrogen atoms)}}\right]}{\left[\dfrac{\text{(yield of } \mathbf{5} \text{ in toluene)}}{2\text{(yield of } \mathbf{6} \text{ in toluene)} \times 3}\right]}$$

(13) J. Kochi and P. E. Mocadlo, *J. Org. Chem.*, **30**, 1134 (1965).
(14) J. K. Kochi and A. Bemis, *J. Amer. Chem. Soc.*, **90**, 4038 (1968).
(15) A. F. Trotman-Dickenson and E. W. K. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

The values calculated in the last column of Table II are listed in the order of increasing reactivity. The number of active hydrogen atoms in ethyl acetate is questionable since the cyclopropyl radical can abstract a hydrogen atom at the position α to the carbonyl as in the case of acetone or at the position α to the alkoxy oxygen as in the case of diethyl ether. Since diethyl ether shows a higher reactivity than that of acetone, the assumption was made that the cyclopropyl radical abstracts a hydrogen atom at the position α to the alkoxy oxygen and two active hydrogen atoms were counted for ethyl acetate. Twelve active hydrogens were counted for cyclohexane by assuming that the axial and equatorial hydrogens show the same reactivity toward the radical. The number of active hydrogen atoms in the other solvents can be deduced clearly. For example, benzene has six and *tert*-butyl alcohol has nine hydrogen atoms, all of which are equally active.

The relative reactivity of thiophenol, chloroform, carbon tetrachloride, and iodine could not be evaluated by the present method, because no **6** was obtained from the decomposition of the peroxide in these reagents.

It is known that benzene is a poor hydrogen donor in hydrogen abstraction reactions due to high carbon–hydrogen bond energy and presumably because the resulting phenyl type radical is not stabilized by resonance. A solvent which has a functional group is more reactive than a saturated hydrocarbon solvent. Among the series of solvents, the reactivities toward hydrogen abstraction increase in the order primary < secondary < tertiary.[16] The effects of substituents have been considered and it becomes clear that any group containing π electrons or any atoms with nonbonded p electrons will favor hydrogen abstraction from the carbon atom to which it is attached by resonance stabilization of the incipient radical. These expectations were confirmed by the results shown in Table II. Benzene was found to be the poorest radical trapping reagent among the solvents, and cyclohexane which has no functional group was next to benzene. *tert*-Butyl alcohol, which has no α-hydrogen and thus would not be expected to show a substitutent effect, showed the same order of reactivity as cyclohexane. Ethyl acetate and diethyl ether exhibited about the same reactivity, presumably due to the same effect of the nonbonded electrons on oxygen. Tetrahydrofuran was more reactive than diethyl ether: this provided the solution to the question posed in the introduction, and is also consistent with the results of Walling and Mintz[17] who reported that tetrahydrofuran is more reactive than diethyl ether toward the *tert*-butoxy radical. Note that the usual order of hydrogen atom reactivity, namely primary < secondary < tertiary, is followed in the series methanol–ethanol–isopropyl alcohol and in the series toluene–ethylbenzene–cumene.

The present method for evaluating relative solvent reactivities seems to give better results than those obtained by the conventional competition technique. The latter can lead to radical induced exchange reactions in the evaluated solvent–carbon tetrachloride mixtures, which complicates the analysis of results.[18] For example, cyclohexane shows an efficient peroxide-induced cross-transfer reaction which converts much of the carbon tetrachloride into chloroform. Since chloroform is a very good hydrogen donor and a very poor chlorine donor, the yield of RH resulting from

$$Cl_3C\cdot + C_6H_{12} \longrightarrow CHCl_3 + \cdot C_6H_{11}$$

$$\cdot C_6H_{11} + CCl_4 \longrightarrow C_6H_{11}Cl + Cl_3C\cdot$$

hydrogen abstraction by R· is much higher than that warranted by the reactivity of cyclohexane itself toward a radical (R)·. Thus, the results show higher reactivity of cyclohexane than is expected.

Selectivity of 9. The order of reactivity of the C–H bond is known to be tertiary > secondary > primary. This difference in reactivity is dependent upon the differences in stability of the corresponding radicals. It is not surprising therefore that a reactive radical (*e.g.*, Cl·, CH_3·) shows little discrimination between different types of bonds, whereas less reactive radicals (*e.g.*, Br·, Cl_3C·) show much greater selectivity in their attack. Comparison of the relative reactivities of benzylic hydrogen listed in Table II with several radicals[8] (shown in Table III) shows that **9** is less selective, more reactive, than the chlorine atom.

Table III. Relative Reactivities of Hydrogen Donors toward Several Radicals

Hydrogen	Bromine atom 40°	Methyl 65°	Phenyl 60°	*tert*-Butoxy 40°	Chlorine atom 40°	**9** 64–65°
Toluene	1	1	1	1	1	1
Ethylbenzene	17.2	4.1	4.6	3.2	2.5	1.77
Cumene	37.0	12.9	9.7	6.9	5.5	2.50

Similary, comparison of the relative reactivities of primary, secondary, and tertiary aliphatic hydrogens (1:3.6:4.2) toward a chlorine atom, with the relative reactivities of the methanol–ethanol–isopropyl alcohol series solvents toward the cyclopropyl radical **9** (1:2.4:3.5) as shown in Table II, further confirms the low selectivity of the cylopropyl radical.

It has been reported that the highly strained cyclic systems would reduce the stability (less selectivity) of the radical. Qualitative indications of the instability of the 1-bicyclo[2.2.1]heptyl radical can be inferred from the product ratio in the thermal decomposition of 1-norbornyldimethylcarbinyl hypochlorite,[19] from the failure of chlorine atoms to abstract bridgehead hydrogens from norbornane,[20] and from the failure of chlorine atoms to abstract the tertiary ring hydrogen from methylcyclopropane[21] or alkycyclopropanes.[22] Quantitative indication of the instability of the highly strained 1-norbornyl radical has been established by a number of workers[23] who estimated that the relative

(16) A. F. Trotman-Dickenson, *Quart. Rev., Chem. Soc.*, **7**, 198 (1953).
(17) C. Walling and M. J. Mintz, *J. Amer. Chem. Soc.*, **89**, 1515 (1967).
(18) D. F. DeTar and D. V. Wells, *ibid.*, **82**, 5839 (1960), and references therein.
(19) F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *ibid.*, **28**, 55 (1963).
(20) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1959).
(21) H. C. Brown and M. Borkowski, *J. Amer. Chem. Soc.*, **74**, 1894 (1952).
(22) J. K. Kochi, P. J. Krusic, and D. F. Eaton, *ibid.*, **91**, 1879 (1969).
(23) D. E. Applequist and L. Kaplan, *ibid.*, **87**, 2194 (1965); J. P. Lorand, J. D. Chodroff, and R. W. Wallace, *ibid.*, **90**, 5266 (1968); R. C. Fort and R. E. Franklin, *ibid.*, **90**, 5267 (1968); L. B. Humphrey, B. Hodgson, and R. E. Pincock, *Can. J. Chem.*, **46**, 3099 (1968).

stability of *tert*-butyl radical and 1-norbornyl radical is 1:0.004, respectively.

Cyclopropyl radicals possess a strained ring system and one would expect that the 1-methyl-2,2-diphenylcyclopropyl radical (**9**) would be a radical of low selectivity, as is observed. However, recently Oda and coworkers[24] have reported that the 2-phenylcyclopropyl radical is more selective than a phenyl radical. A rational explanation awaits further experimental evidence.[12]

Experimental Section

Instruments. Infrared spectra were obtained with a Perkin-Elmer Model 137 or a Model 257 infrared spectrophotometer. Solution spectra were run on 3% solutions of either carbon tetrachloride or chloroform in a 0.5-mm sodium chloride cell. The 1601-cm^{-1} peak of polyethylene was used for calibration of chart paper. Ultraviolet spectra were run on a Cary 14 recording spectrometer using 1-cm quartz cells.

Rotations were measured at the 546.1-mμ line of mercury on a Bendix-Ericson Model 987 ETL/NPL polarimeter. Nuclear magnetic resonance spectra were obtained on a Varian Associates A-60 spectrometer using tetramethylsilane as an internal standard. Mass spectra were obtained from a Nuclide 12-90 G 1.5 magnetic deflection mass spectrometer.

Melting points were determined in capillary tubes using a Mel-Temp apparatus with a calibrated thermometer.

Vapor phase chromatography was conducted on a F & M Model 500 programmed temperature gas chromatograph with a thermistor detector, using helium as a carrier gas. All columns were formed from $^1/_4$-in. o.d. copper tubing.

Carbon and hydrogen analyses were run by Dr. M. Mitsui's Laboratory, Department of Agricultural Chemistry, Kyoto University, Kyoto, Japan.

1-Methyl-2,2-diphenylcyclopropanecarbonyl Peroxide (2). An ethereal hydrogen peroxide solution was prepared by slowly adding 49.2 g of 90% hydrogen peroxide to 200 ml of ice-cold ether with subsequent removal of water by drying over sodium sulfate.

In a three-necked flask equipped with a magnetic stirrer and thermometer, and cooled by means of an ice bath, were placed 300 ml of ether, 17.0 g (0.0825 mol) of *N,N'*-dicyclohexylcarbodiimide, and 100 ml of the ethereal hydrogen peroxide solution. A solution of 20.0 g (0.0793 mol) of 1-methyl-2,2-diphenylcyclopropanecarboxylic acid in 100 ml of ethylene chloride was added slowly with stirring. The resulting mixture was stirred at ice-bath temperature for 5 hr and then kept in a refrigerator overnight. The mixture was filtered and the filtrate was washed with cold saturated ammonium sulfate solution, cold saturated aqueous sodium bicarbonate solution, and cold saturated sodium chloride solution. The washed solution was dried over sodium sulfate and the solvent was completely removed under reduced pressure at room temperature. Two recrystallizations from ether gave 12.5 g (67.8% yield) of **2** as white needles, mp 130.5° dec. Iodometric titration indicated that it was 98.3% pure. The peroxide showed significant infrared absorption ($CHCl_3$) at 1795 and 1770 (s) cm^{-1}; nmr ($CDCl_3$) 7.5–7.0 (10 H, multiplet, aromatic), two doublets at 2.25 and 1.5 (2 H, 5 cps, ring), 1.2 ppm (3 H, singlet, methyl).

Anal. Calcd for $C_{34}H_{30}O_4$: C, 81.25; H, 6.02. Found: C, 81.04; H, 6.20.

2,2-Diphenylcyclopropanecarbonyl peroxide (1) was prepared from 2,2-diphenylcyclopropanecarboxylic acid by the method described above for the preparation of **2**. The yield was 50%; mp 124° dec; 98.7% purity; the infrared spectrum ($CHCl_3$) showed 1790 and 1775 (s) cm^{-1}; nmr ($CDCl_3$) 7.46–6.9 (10 H, multilet, aromatic), 2.47 (H, quartet, 6 and 8 cps, α-hydrogen), 2.22 (H, quartet, 6 and 5 cps, methylene), 1.72 ppm (H, 8 and 5 cps, quartet, methylene).

1-Bromo-2,2-diphenylcyclopropanecarbonyl peroxide (3) was prepared from 1-bromo-2,2-diphenylcyclopropanecarboxylic acid by the method described above for preparation of **2**. The yield was 67.7%; mp 111° dec; 97.2% purity; the infrared spectrum ($CHCl_3$) showed 1790 and 1765 (s) cm^{-1}; nmr ($CDCl_3$) 7.5–7.0 (10 H, multiplet, aromatic), two doublets at 2.7 and 2.0 ppm (2 H, 6 cps, ring).

General Procedure for the Thermal Decomposition of Peroxides. Solvents were purified by conventional methods. A peroxide solution (0.02 *M*) was placed in a glass bomb and the contents were swept with dry argon gas and sealed and immersed in a thermostated oven at 64–65° for 24 hr. In the case of solvents which were soluble in water, the solvent was carefully distilled off and the residue dissolved in ether. The ethereal solution was extracted three times with aqueous sodium bicarbonate, washed with water, and dried over magnesium sulfate. The ether was carefully removed by distillation leaving an oily neutral residue.

Vpc Analysis. The acid-free neutral residue was analyzed by gas chromatography with 9 × $^1/_4$ in. 10% SE 30 on 60–80 Chromosorb P column. Quantitative analyses of **5** and **6** were carried out at 100 and 250°, respectively, using naphthalene as an internal standard.[25] The average values of 3–6 runs of each sample are summarized in Table II. The SE 30 and/or 4-ft 20% EGIP on Chromosorb W were used at 200° for collection of **5** and also for identification of 1,1-dimethyl-2,2-diphenylethylene and other cyclopropyl derivatives.

The best procedure for isolation of **5** or the corresponding deuteriocyclopropyl compounds was as follows. The neutral portion was subjected to thin layer chromatography on silica gel using hexane as the developing solvent. The main broad band between R_f 0.25 and 0.39 was extracted, and purified by vpc using an EGIP column at 200°. The mass spectrum of **5** showed 18% relative intensity at *m/e* 209 (P + 1) compared to molecular ion 208 ($C_{16}H_{16}^+$, also the base peak), 21.4% relative intensity a *m/e* 194 compared to 193 ($C_{16}H_{16}^+ - CH_3$).

The combined sodium bicarbonate solution was cooled by means of an ice bath, acidified with cold dilute hydrochloric acid, and extracted three times with ether. The ethereal solution was washed with water and dried over magnesium sulfate. The ether was stripped under reduced pressure to give **4**. Yields are summarized in Table II. The infrared spectrum of the acid was identical with that of an authentic sample,[2,4] and a mixture melting point with an authentic sample showed no depression.

Isolation of 1,1,6,6-Tetraphenyl-2,5-dimethyl-1,5-hexadiene (6) and 2-Methyl-4,4-diphenyl-Δ^2-γ-butyrolactone (7). The oily neutral portion, which was separated from the reaction mixture from the decomposition of **2** in benzene, was adsorbed onto an alumina column. The column was washed successively with low-boiling petroleum ether, then benzene. Removal of petroleum ether yielded a mixture of **5** and **6**. Recrystallization from carbon tetrachloride gave mp 140–143° (lit.[26] mp 145–146°). The yields of **7** obtained in various solvents are summarized in Table II. The uv spectrum (C_2H_5OH) showed λ_{max} 245 mμ (ϵ 23,900); nmr (CCl_4) 7.05 (10 H, singlet, aromatic), 2.26 (3 H, singlet, methyl), 1.6 ppm (2 H, singlet, methylene).

Anal. Calcd for $C_{32}H_{30}$: C, 92.75; H, 7.25. Found: C, 92.75; H, 7.41.

Removal of benzene from the eluent solution left an oily residue which on recrystallization from pentane gave **7** as a microcrystalline white solid, mp 68–69°. The infrared spectrum (CCl_4) showed a characteristic α,β-unsaturated γ-lactone absorption at 1770 cm^{-1} (s); nmr (CCl_4) 7.57 (H, singlet, vinylic), 7.25 (10 H, singlet, aromatic), 1.87 ppm (3 H, singlet, methyl). The infrared and nmr spectra were identical with an authentic sample which was synthesized from dimethyl succinate (*vide infra*). A mixture melting point gave no depression.

Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.60; H, 5.68. Found: C, 81.55; H, 5.81.

1,1,6,6-Tetraphenyl-1,5-hexadiene. This compound was isolated from the decomposition of **1** in benzene at 80°. The procedure was similar to that described above for isolation of **6**. Recrystallization from ether and then acetone gave white needle crystals, mp 102–104°. The uv spectrum (C_2H_5OH) showed λ_{max} 255 (ϵ 25,600); nmr (CCl_4) 7.13 (10 H, singlet, aromatic), 6.0 ppm (H, singlet, vinyl), 2.25 ppm (2 H, 4 cps, methylene).

Anal. Calcd for $C_{30}H_{26}$: C, 93.26; H, 6.25. Found: C, 93.00; H, 6.28.

1,1,6,6-Tetraphenyl-2,5-dibromo-1,5-hexadiene. This compound was isolated from the decomposition of **3** in benzene at 80°. The procedure was similar to that described above for isolation of **2**. Recrystallization from ether gave mp 162–163°. The uv spectrum (C_2H_5OH) showed λ_{max} 245 (ϵ 20,200). The nmr spectrum was consistent with the structure.

Anal. Calcd for $C_{30}H_{24}Br_2$: C, 66.2; H, 4.45. Found: C, 66.1; H, 4.57.

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Preparation of 2-Methyl-4,4-diphenyl-Δ^2-γ-butyrolactone (7). 2-Methyl-3-carbomethoxy-4,4-diphenyl-3-butenoic acid was prepared by the method described in the literature.[27]

A solution of 21.5 g of the above acid, 330 ml of acetic acid, 215 ml of 49% hydrobromic acid, and 108 ml of water was refluxed for 6 hr. The acidic portion was worked up in the usual way and recrystallization from a methanol–water mixture gave a 21.2% yield of 2-methyl-4,4-diphenyl-3-butenoic acid, mp 104.5–105°. The infrared spectrum showed a broad band 3500~2500 (broad) and 1720 (s) cm^{-1}; nmr (CCl_4) 7.7–7.0 (10 H, multiplet, aromatic), 6.06 (H, doublet, vinyllic hydrogen), 3.6–3.0 (H, multiplet, tertiary hydrogen), 1.29 ppm (3 H, doublet, 7 cps, methyl).

Bromine (1 ml) was added slowly to a solution of 0.194 g of the above acid in 50 ml of saturated aqueous solution of bicarbonate. The mixture was stirred at room temperature for 1 hr and extracted with ether. The ethereal solution was washed with water and dried over magnesium sulfate. The ether was removed by distillation leaving a solid residue. Recrystallization of the residue from pentane gave a 92.8% yield of 2-methyl-3-bromo-4,4-diphenylbutyrolactone, mp 130–132°. The ir spectrum (CCl_4) showed a characteristic lactone absorption at 1800 cm^{-1} (s). The nmr spectrum (CCl_4) showed that the lactone was a mixture of cis and trans isomers: 5.45 (0.355 H, doublet, 4 cps, benzylic) and 4.63 (0.644 H, doublet, 12 cps, benzylic), 7.9–7.15 (10 H, multiplet, aromatic), 3.15–2.5 (1 H, multiplet, α-hydrogen), 1.34 (3 H, doublet, 7 cps, methyl).

A solution of 0.43 g of the above lactone, 1 g of potassium hydroxide, 30 ml of methanol, and 9 ml of water was refluxed for 3.5 hr. The methanol was distilled off, a small amount of ice water was added, and the reaction mixture was acidified with cold dilute hydrochloric acid and extracted with ether. The ethereal layer was washed with saturated aqueous sodium bicarbonate and water and dried over magnesium sulfate. Removal of the ether gave **7**, which after recrystallization from pentane had mp 68–69°.

Isolation of Methyl 1-Methyl-2,2-diphenylcyclopropanecarboxylate. The neutral portion which was separated from the decomposition of **2** in methanol was chromatographed on an alumina column. The alumina was eluted with low-boiling petroleum ether until no more material was found in the solvent. After evaporating the solvent, the methyl ester was collected by vpc using a 2-ft 20% CES on Chromosorb W column at 125°, in a yield of 27.7%, mp 89–90°. The ir and nmr spectra were identical with those of an authentic sample which was prepared from methyl methacrylate and diphenyldiazomethane. A mixture melting point gave no depression.

Decomposition of 2 in Carbon Tetrachloride. The procedures for decomposition, separation of the neutral fraction, isolation of **5**, and quantitative analysis of the products by vpc were the same as described in the general procedure. 1-Chloro-1-methyl-2,2-diphenylcyclopropane was isolated by the following procedure: the neutral portion of the reaction mixture was chromatographed on an alumina column using low-boiling petroleum ether as an eluent. Upon evaporation of the petroleum ether, the residue solidified to yield 19.3% of 1-chloro-1-methyl-2,2-diphenylcyclopropane, mp 65–65.5°. The infrared and nmr spectra were identical with those of an authentic sample.[2,3] A mixture melting point gave no depression. Decomposition of (+)-**2**, $[\alpha]_{Hg}^{23}$ 5.1 (70.3% optical purity, prepared from (−)-**4**, $[\alpha]_{Hg}^{23}$ 30.0) gave (−)-1-chloro-1-methyl-2,2-diphenylcyclopropane, $[\alpha]_{Hg}^{23}$ 1.05 (*c* 2.85, $CHCl_3$).

Decomposition of 2 in Benzene-d_6. The procedures for the decomposition of the peroxide and the isolation of the cyclopropyl hydrocarbon fraction were the same as described in the general procedure. Mass spectrum of the product showed *m/e* 209 ($C_{16}H_{15}D^+$, base peak), 210 (P + 1, relative intensity 21.4%).

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A Kinetic and Equilibrium Study of the Hydrogen Bond Dimerization of 2-Pyridone in Hydrogen Bonding Solvents[1]

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Abstract: Rate and equilibrium constants for the hydrogen bond dimerization of 2-pyridone in chloroform–dimethyl sulfoxide (DMSO) and in CCl_4–DMSO mixtures at various DMSO concentrations have been determined by ultrasonic attenuation, ultraviolet, infrared, and nmr measurements. For the former solvent system, the association rate constants were characteristic of a diffusion-controlled process ($k_f \sim 10^9\ m^{-1}\ sec^{-1}$). The equilibrium dissociation constants increased with increasing DMSO content of the solvent, suggesting that the dissociation rate constant is a measure of solvent competition for hydrogen bonds. The values of standard enthalpy changes for the reactions, calculated from the ultrasonic data, also support this interpretation: $\Delta H°$ changes from −6 to −4 kcal/mol as DMSO is increased from 0.67 to 2.26 *m*. For the latter solvent system, very different behavior is observed. The association rate constant is $<10^9\ m^{-1}\ sec^{-1}$ in all cases, indicating that the formation of dimers is not diffusion controlled. The dissociation rate constant increases to a limiting value of $\sim 3.3 \times 10^8\ sec^{-1}$ as the DMSO content is increased. A mechanism, involving 2-pyridone–DMSO complexes, is postulated and leads to the conclusion that solvation–desolvation of 2-pyridone by DMSO becomes rate limiting. The implication of these findings for biological processes is considered.

The hydrogen bond is a significant factor in the structure and function of biological macromolecules.[2-4] Many equilibrium studies have been made of both biological and model systems. Relatively recently, the dynamics of these interactions have also been studied and information is now available on the rates of formation and breakdown of most types of commonly occurring hydrogen bonds.[4] Virtually all the kinetic data have been obtained by studies of the dimerization of simple chemical compounds such as benzoic acid,[5] ϵ-caprolactam,[6] and analogs of the bases of nucleic

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