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Relative Reactivity of Maleic Anhydride and Sulfur Dioxide in 1,4-Addition Reactions to 2,3-Dimethyl-1,3-butadiene

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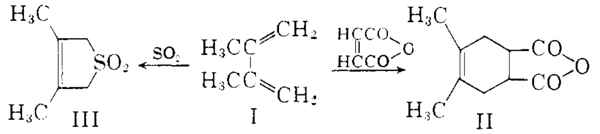
The relative reactivity of maleic anhydride and sulfur dioxide in their reactions with 2,3-dimethyl-1,3-butadiene to form the Diels–Alder adduct and cyclic sulfone was estimated by competitive relative rate measurements. Results were calculated for reactions in various solvents at 0°, 27°, (approx.), and 50° as ratios of second-order rate constants, k_1/k_2, Diels–Alder reaction/sulfone reaction; these constants were not measured individually. Values for this ratio ranged from 39.3 to 363 as reactant ratio, solvent and temperature were varied. Thus maleic anhydride is more reactive than sulfur dioxide in 1,4-addition under all conditions studied. The effect of solvent, particularly on the sulfone reaction, is interpreted in terms of dielectric constant and coördination of the solvent with sulfur dioxide. Increasing dielectric constant decreases the rate ratio as a straight line function for reactions in benzene, chloroform and liquid sulfur dioxide. In mesitylene and the ether solvents, the ratios were higher than expected, according to dielectric constant, because of sulfur dioxide–solvent interaction. Increased temperature relatively favors the sulfone reaction. In tetrahydrofuran solution this is partially attributed to the dissociation of solvated sulfur dioxide. Estimation of the differences in heats of activation for the two reactions indicated values 1.5–5.0 kcal. greater for the sulfone reaction.

1,3-Dienes may react with maleic anhydride to form Diels–Alder adducts and with sulfur dioxide to form cyclic sulfones. The literature on these reactions shows that maleic anhydride is probably more reactive than sulfur dioxide. It was the purpose of this work to measure the reactivity difference by means of competitive reactions.

2,3-Dimethyl-1,3-butadiene (I), maleic anhydride and/or sulfur dioxide were allowed to react in various solvents at 0°, approx. 27° and 50°



Preliminary experiments showed that the yield of the Diels–Alder adduct, 1,2-dimethyl-1-cyclohexene-4,5-dicarboxylic anhydride (II),[2] was almost independent of the nature of the solvent, but the sulfone reaction was strongly affected by the solvent. Therefore, five solvents of varying effects were selected: tetrahydrofuran, mesitylene, benzene, bis-(2-chloroethyl) ether and chloroform.

The yield of II from equimolar quantities of reactants in all solvents at room temperature for 36–48 hours varied from 90 to 100% (Table I).[3]

TABLE I[a]

DIELS–ALDER REACTIONS AT APPROX. 27° IN VARIOUS SOLVENTS

Expt.	Solvent	—Molarity of— I	Maleic anhydride	Time, hr.	Yield of II, %
1	Tetrahydrofuran	0.94	0.92	36	90
2	Mesitylene	.96	.92	48	97
4	Benzene	.87	.87	36	95
5	Chloroethyl ether	1.02	1.02	48	98
6	Chloroform	0.98	0.93	48	99

[a] Also see Table VI.

Addition of sulfur dioxide to 2,3-dimethylbutadiene gives 3,4-dimethyl-2,5-dihydrothiophene 1,1-dioxide (III).[4] The yields of III from equimolar quantities of reactants at room temperature for 36–48 hours vary from 4 to 62% (Table II). The sulfone yield increases in the following series of solvents: tetrahydrofuran, mesitylene, benzene, bis-(2-chloroethyl) ether and chloroform.

TABLE II[a]

SULFONE REACTIONS AT APPROX. 27° IN VARIOUS SOLVENTS

Expt.	Solvent	—Molarity of— I	SO_2	Time, hr.	Yield of III, %
7	Tetrahydrofuran	1.0	0.94	48	4.1
11	Mesitylene	1.01	.90	48	11.5
16	Benzene	0.98	.89	48	25.3
19	Chloroethyl ether	0.99	.90	48	50
21	Chloroform	1.01	.92	48	62

[a] Also see Table VII.

With the behavior of the individual reactions established, competitive reactions were carried out in the same solvents at room temperature for 48 hours. Approximately 1 molar concentrations of I and maleic anhydride were used, and the concentration of sulfur dioxide was varied from 1 to 10 molar. The reaction product was vacuum distilled, III was estimated by measuring the sulfur dioxide formed on heating,[5] and II was hydrolyzed to the dicarboxylic acid IV which was separated and measured acidimetrically.

Diels–Alder reactions are known to be second order,[6] and the reasonable assumption was made that the sulfone reaction was also second order. From the quantities of reactants taken and products found, the ratio of the rate constants, k_1/k_2, was calculated[7] (Table III)

$$k_1/k_2 = \frac{\log (1 - x/a)}{\log (1 - y/b)} \qquad (1)$$

where

k_1 = rate constant of the Diels–Alder reaction
k_2 = rate constant of the sulfone reaction
x = moles of II formed
y = moles of III formed
a = initial moles of maleic anhydride
b = initial moles of sulfur dioxide

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[1] A Sherwin-Williams fellowship granted to A. L. Endrey in 1954–1955 is gratefully acknowledged.

[2] E. H. Farmer and F. L. Warren, *J. Chem. Soc.*, 897 (1929).

[3] The results given in Tables I–IX were satisfactorily verified by duplicate experiments.

[4] H. J. Backer and J. A. Bottema, *Rec. trav. chim.*, **51**, 294 (1932).

[5] O. Grummitt, A. E. Ardis and J. Fick, THIS JOURNAL, **72**, 5167 (1950).

[6] L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 6284 (1955).

[7] T. L. Davis and J. M. Farnum, *ibid.*, **56**, 883 (1934).

TABLE III

RATIOS OF RATE CONSTANTS IN COMPETITIVE REACTIONS (APPROX. 27°)[a]

Expt.	Mole ratios: Reactants I/mal. anhy./SO_2/solvent	Mole ratios: Products II/III	k_1/k_2
	In tetrahydrofuran		
22	1/1/0.95/10.3	127.1	363
23	1/1/1.9/9.1	57.7	300
24	1/1/5.3/7.5	14.5	173
25	1/1/9.2/4.7	5.1	89.6
	In mesitylene		
26	1/1/0.86/5.7	53.1	154
27	1/1/2.0/5.1	29.6	135
28	1/1/4.8/4.4	9.8	96
29	1/1/9.5/2.9	4.4	75.5
	In benzene		
30	1/1/0.91/9.2	45.1	117
31	1/1/0.94/9.1	41.8	114
32	1/1/1.9/8.2	18.5	88.6
33	1/1/4.6/7.1	7.7	73.0
34	1/1/10.0/4.3	3.4	51.0
	In chloroethyl ether		
35	1/1/0.91/7.0	36.2	87.7
36	1/1/1.7/6.1	18.3	75.3
37	1/1/4.8/5.2	6.6	63.6
38	1/1/10.9/3.2	2.7	48.4
	In chloroform		
39	1/1/1.2/10.3	26.8	77.9
40	1/1/2.1/9.1	13.7	67.2
41	1/1/4.9/7.5	5.3	55.0
42	1/1/8.6/4.9	3.1	46.1
	In liquid SO_2		
43	1/1/18.0/—	1.5	39.3

[a] Also see Table VIII.

The ratios of rate constants, 363–39.3, shows that maleic anhydride is always more reactive than sulfur dioxide under these conditions. Maleic anhydride is relatively most reactive when equimolar quantities of diene, maleic anhydride and sulfur dioxide react in tetrahydrofuran (expt. 22). Maleic anhydride is least reactive when the organic solvent is replaced by a large excess of sulfur dioxide (expt. 43).

In seeking an explanation for the strong effect of solvent on the sulfone formation and competitive reactions, differences in dielectric constant of the reaction media were considered. The general effect of dielectric constant on reaction rates is given by the Laidler–Eyring equation[8]

$$\ln k = \ln k_0 - \frac{1}{k_B T}\frac{D-1}{2D+1}\left[\frac{\mu^2 A}{r_A{}^3} + \frac{\mu^2 B}{r_B{}^3} - \frac{\mu^2 C}{r_C{}^3}\right] \quad (2)$$

where

k = apparent rate constant
k_0 = rate constant at $D = 1$
D = dielectric constant
k_B = Boltzmann constant
T = absolute temperature
μ_A = dipole moment of reactant A
r_A = molecular radius of reactant A
μ_B = dipole moment of reactant B
r_B = molecular radius of reactant B
μ_C = dipole moment of the activated complex
r_C = molecular radius of the activated complex

Application of equation 2 to the Diels–Alder and sulfone competitive reactions gives

$$\ln (k_1/k_2) = \ln (k_1/k_2)_0 - \frac{1}{k_B T}\frac{D-1}{2D+1}\left[\frac{\mu_1{}^2}{r_1{}^3} - \frac{\mu_2{}^2}{r_2{}^3} - \frac{\mu_3{}^2}{r_3{}^3} - \frac{\mu_4{}^2}{r_4{}^3}\right] \quad (3)$$

where

k_1/k_2 = the apparent ratio of rate constants
$(k_1/k_2)_0$ = the ratio of rate constant at $D = 1$
r_1 = molecular radius of maleic anhydride
μ_1 = dipole moment of maleic anhydride
r_2 = molecular radius of the activated complex in the Diels–Alder reaction
μ_2 = dipole moment of the activated complex in the Diels–Alder reaction
r_3 = molecular radius of sulfur dioxide
μ_3 = dipole moment of sulfur dioxide
r_4 = molecular radius of the activated complex in the sulfone reaction
μ_4 = dipole moment of the activated complex in the sulfone reaction

For a constant temperature equation 3 can be simplified (C is a constant)

$$\log (k_1/k_2) = \log (k_1/k_2)_0 - \frac{D-1}{2D+1}C \quad (4)$$

According to 4, a plot of log (k_1/k_2) against $(D - 1)/(2D + 1)$ gives a straight line. This prediction cannot be tested exactly because the dielectric constant of the reaction mixture changes as the reaction progresses, and the dielectric constants of II and III are not known. As an approximation, the dielectric constants of the initial reaction mixtures were estimated from published dielectric constants of I, sulfur dioxide, maleic anhydride and the solvents on the assumption that the solutions were ideal. These data are summarized in Table IV and plotted in Fig. 1.

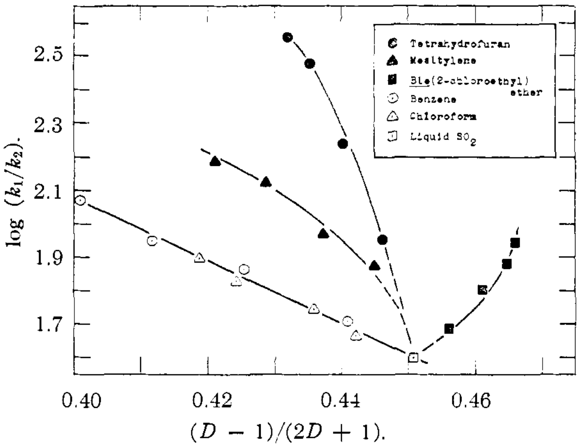

Fig. 1.—Change in the ratio of rate constants with dielectric constant of the solvent.

The data obtained in benzene, chloroform and liquid sulfur dioxide solutions form a straight line. However, the reactions in tetrahydrofuran, mesitylene and chloroethyl ether do not conform to equation 4, and these data give three different curves. The straight line for the "normal" solvents, *i.e.*, benzene, chloroform and liquid sulfur

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[8] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 419.

TABLE IV

RELATION BETWEEN RATIO OF RATE CONSTANTS AND DIELECTRIC CONSTANT

Expt.	k_1/k_2	$\log (k_1/k_2)$	D (init. reacn.)	$\frac{D-1}{2D+1}$
	In tetrahydrofuran ($D = 7.39$)[a]			
22	363	2.560	10.55	0.4320
23	300	2.477	11.1	.4355
24	173	2.238	12.1	.4405
25	89.6	1.952	13.32	.4460
	In mesitylene ($D = 2.356$)[a]			
26	154	2.188	8.99	0.4210
27	135	2.130	10.01	.4286
28	96.0	1.982	11.41	.4372
29	75.5	1.878	13.10	.4449
	In benzene ($D = 2.284$)[a]			
30	117	2.0682	7.05	0.4007
31	114	2.0569	7.11	.4015
32	88.6	1.9474	8.00	.4118
33	73.0	1.8633	9.57	.4255
34	51.0	1.7076	12.15	.4407
	In chloroethyl ether ($D = 21.2$)[a]			
35	87.7	1.943	21.5	0.4659
36	75.3	1.877	20.9	.4649
37	63.6	1.803	19.0	.4615
38	48.4	1.685	16.65	.4563
	In chloroform ($D = 4.806$)[a]			
39	77.9	1.8915	8.74	0.4188
40	67.2	1.8274	9.45	.4246
41	55.0	1.7404	11.19	.4358
42	46.1	1.6637	12.49	.4423
	In liquid sulfur dioxide ($D = 13.6$)[a]			
43	39.3	1.5944	14.82	0.4510

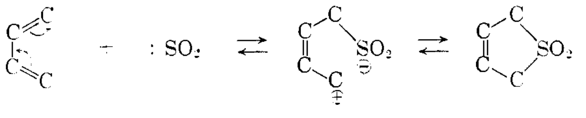
[a] Dielectric constants of the solvents are at approximately 25°.

dioxide, is expressed by equation 5 (found by the method of least squares)

$$\log (k_1/k_2) = 5.806 - 9.34 \frac{D-1}{2D+1} \quad (5)$$

Thus sulfone formation is favored by increasing dielectric constant of the reaction medium. Since the rate of the Diels-Alder reaction also probably increases with increasing dielectric constant, as is true of cyclopentadiene-benzoquinone[9a] and cyclohexadiene-maleic anhydride,[9b] it appears that the extent of change is much greater for the sulfone reaction under competitive conditions.

The favorable effect of polar solvents on the sulfone reaction is in agreement with a polar mechanism of addition in which sulfur dioxide is an electrophilic reactant[5]



It is believed that the abnormal solvents—mesitylene, tetrahydrofuran and chloroethyl ether—react as Lewis bases with sulfur dioxide and thus decrease its effective concentration. Sulfur dioxide addition compounds have been reported for various oxygenated organic compounds,[10a] benzene and alkylated benzenes.[10b] The decreased effective concentration of sulfur dioxide makes the ratio of reaction rates higher than predicted by the dielectric constant (equation 4).

Maleic anhydride also reacts with certain of these solvents. Equilibrium constants for maleic anhydride-benzene reaction are 0.60–0.85 at 25°.[11] The extent of this reaction is slightly greater than that of sulfur dioxide-benzene which has an equilibrium constant (25°) of 0.47.[10b] Mesitylene is more reactive with sulfur dioxide than with maleic anhydride; equilibrium constants (25°) are 2.11[10b] and 0.94–1.3, respectively.[11]

Two consecutive reactions that would affect the yields from the competitive reactions were considered: (1) dissociation of the sulfone and (2) displacement of sulfur dioxide from the sulfone by maleic anhydride. Model experiments showed that neither of these complicating reactions occurred. Sulfone III is not dissociated when refluxed in water for 1 hour.[12] Maleic anhydride and III did not react in tetrahydrofuran, chloroethyl ether or benzene solution during 6 days at room temperature.

To determine the effect of temperature on the relative reactivity of maleic anhydride and sulfur dioxide, competitive reactions were run at 0°, 27° (approx.), and 50° (Table V). Chloroform was taken as a typical normal solvent and tetrahydrofuran as an abnormal type. In both solvents the lower temperature of 0° increased the ratio of rate constants and the higher temperature of 50° decreased the ratio. Therefore higher temperatures in the range of 0–50° relatively favor the addition of sulfur dioxide.

TABLE V

EFFECT OF TEMPERATURE ON THE RATIO OF RATE CONSTANTS[a]

		Mole ratios		
Expt.	t, °C.	Reactant I/mal. anhyd./SO_2/solvent	Products II/III	k_1/k_2
		In chloroform		
44	0	1/1/0.94/10.5	37.3	90.4
45	0	1/1/0.97/10.3	34.1	86.5
39	27[b]	1/1/1.2/10.3	26.8	77.9
46	50	1/1/0.90/10.2	23.1	55.9
47	50	1/1/0.93/10.2	23.6	59.4
		In tetrahydrofuran		
48	0	1/1/4.9/7.7	43.7	520
49	0	1/1/5.1/7.6	41.7	512
24	27[b]	1/1/5.3/7.5	14.5	173
50	50	1/1/4.8/7.6	11.0	123.5
51	50	1/1/5.0/7.5	10.8	125

[a] Also see Table IX. [b] Approximately.

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(9) (a) R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 236 (1938); (b) Y. Yukawa and A. Isohisa, *Mem. Inst. Sci. Ind. Research Osaka Univ.*, **10**, 191 (1953); *C. A.*, **48**, 7598 (1954).

(10) (a) N. F. Albertson and W. C. Fernelius, THIS JOURNAL, **65**, 1687 (1943). (b) L. J. Andrews and R. M. Keefer, *ibid.*, **73**, 4169 (1951).

(11) L. J. Andrews and R. M. Keefer, *ibid.*, **75**, 3777 (1953).

(12) The thermal stability of III is indicated by earlier work: equilibrium constants for the formation of butadiene sulfone are 175–180 (100°), 304 (90°); L. R. Drake, S. C. Stowe, and A. M. Partansky, *ibid.*, **68**, 2521 (1946). The decomposition temperature of III is higher than that of butadiene sulfone.[5]

TABLE VI

DIELS-ALDER REACTIONS

Expt.	Solvent (g.)	I G.	I Mole	Maleic anhydride G.	Maleic anhydride Mole	Soln. vol., ml.	Time, hr.	Product M.p., °C.	Product G.	Product %
1	Tetrahydrofuran (39.5)	3.9	0.048	4.9	0.05	53.2	36	195[a]	8.5	90
2	Mesitylene (31.7)	3.55	.043	4.1	.042	45.3	48	76-77	7.3	97
3	Carbon tetrachloride (75.8)	4.1	.050	4.7	.048	56.3	36	77-78	8.8	100
4	Benzene (52.8)	5.1	.062	6.1	.062	71.2	36	200[a]	11.7	95
5	Chloroethyl ether (44.5)	3.55	.043	4.25	.043	42.6	48	75-76	7.7	98
6	Chloroform (54.3)	3.55	.043	4.0	.041	44.1	48	76-77	7.4	98

[a] Measured as the acid, then converted to the anhydride, m.p. 76-77°.

TABLE VII

SULFONE REACTIONS

Expt.	Solvent (g.)	I G.	I Mole	SO_2 G.	SO_2 Mole	Vapor phase SO_2, mole	Soln. vol., ml.	Time, hr.	Product M.p., °C.	Product G.	Product %
7	Tetrahydrofuran (32.4)	3.55	0.043	2.90	0.045	0.0045	43.5	48	115-125[a]	0.26	4.1
11	Mesitylene (30.9)	3.55	.043	2.75	.043	.0063	42.7	48	130-132	0.72	11.5
13	Carbon tetrachloride (59.1)	3.55	.043	2.80	.044	.0049	44	48	133-134	1.12	17.4
16	Benzene (32.6)	3.55	.043	2.80	.044	.0046	44.2	48	133-134	1.62	25.3
19	Chloroethyl ether (45.0)	3.55	.043	2.90	.045	.0060	43.8	48	134-135	3.18	50
21	Chloroform (55.2)	3.55	.043	2.65	.041	.0041	42.8	48	135-136	3.91	62

[a] Mixed m.p. with III, 115-130°.

If the change in dielectric constant with temperature is assumed to be insignificant, the difference between the energies of activation for the Diels-Alder and sulfone reactions can be calculated

$$\ln (k_1/k_2)' - \ln (k_1/k_2)'' = (E_1 - E_2)(1/T'' - 1/T') \quad (6)$$

$\ln (k_1/k_2)'$ = ratio of rate constants at T' absolute temp.
$\ln (k_1/k_2)''$ = ratio of rate constants at T'' absolute temp.
E_1 = energy of activation for the Diels-Alder reacn.
E_2 = energy of activation for the sulfone reacn.

which was derived from the Arrhenius equation.[13]

In the range of 0 to 50°, $E_1 - E_2$ in chloroform is 1500 ± 200 cal.; in tetrahydrofuran, 5000 ± 40 cal.[14] The larger difference in tetrahydrofuran reflects the greater decrease of k_1/k_2 with increased temperature. This can be interpreted as the result of a higher effective concentration of sulfur dioxide because increased temperature has lowered the concentration of solvated sulfur dioxide.

Experimental

Preparation of Materials.—2,3-Dimethyl-1,3-butadiene (I) was prepared by catalytic dehydration of pinacol over activated alumina at 460-510° (20-100 mm.).[15] The typical yield was 50%; $n^{20}D$ 1.4387, reported[16] 1.4393. The main by-product, pinacolone, was recycled to give more diene. If pinacolone is the only impurity, the refractive index indicates that I is 99% pure.

Maleic anhydride (Eastman Kodak Co.), after distilling at 195°, melted 56-58°; sulfur dioxide (Ohio Chemical) was purified by bubbling through concentrated sulfuric acid, then passed through glass wool.

Tetrahydrofuran (Matheson, Coleman and Bell) was refluxed over sodium for 12 hours, fresh sodium was added several times, and distilled to collect the 66° fraction. Bis-(2-chloroethyl) ether (Eastman Kodak Co.) was washed with 10% ferrous sulfate solution, water, dried over calcium sulfate and distilled at 94° (33 mm.).

Chloroform (Merck reagent) was purified.[17] Benzene (Merck reagent) and anisole were dried by refluxing over sodium and distilled. Mesitylene (Eastman Kodak Co.) was washed with 75% sulfuric acid, water, dried over calcium sulfate, and distilled at 162-163°, reported[18] 164.5-164.8°.

3,4-Dimethyl-2,5-dihydrothiophene 1,1-Dioxide (III).[5]—In a 400-ml. pressure bottle 4.9 g. (0.06 mole) of I and 43.2 g. (0.67 mole) of sulfur dioxide were allowed to stand for 12 hours at room temperature. Unreacted material was evaporated at room temperature under suction. The residue, 7.5 g. (88%), was recrystallized from 200 ml. of hot water and dried in a desiccator with calcium sulfate; m.p. 134.5-135.5°, reported[5] 135-136°.

2,3-Dimethyl-1,3-butadiene Polysulfone.—In a 400-ml. pressure bottle 9 g. (0.11 mole) of I, 12 g. (0.19 mole) of sulfur dioxide and 0.2 g. silver nitrate catalyst were allowed to react for 2 hours at room temperature. The non-volatile residue was ground, washed with ethanol, and dried in air to give 15.2 g., 97%. The polysulfone is insoluble in organic solvents and in water. It darkens at about 215° when heated in a melting point tube. In refluxing trimethylbenzene (160°) the polymer slowly decomposes and sulfur dioxide is liberated.

***cis*-1,2-Dimethyl-1-cyclohexene-4,5-dicarboxylic Anhydride (II) and Acid IV.**—Compound II was prepared by allowing maleic anhydride to react with a 10% excess of I in benzene or carbon tetrachloride (about two molar) at room temperature for several days. Solvent and excess I were distilled *in vacuo*. Yields were quantitative, m.p. 77-78°, reported[19] 78-79°.

The anhydride II was converted to the sodium salt of IV by boiling with an equivalent amount of 10% sodium hydroxide. After cooling, IV was precipitated with excess hydrochloric acid, filtered, washed with water, recrystallized from ethanol-water and dried in a desiccator with calcium sulfate; m.p. 199-200° dec., reported[19] 204° dec.; calcd. neut. equiv. 99.1, found 99.1. Compound II was regenerated by boiling IV with ten times the equivalent amount of acetic anhydride for 15 minutes. Acetic acid and excess anhydride were vacuum distilled to leave II in quantitative yield; m.p. 78-80°.

Diels-Alder and Sulfone Reactions in Various Solvents.—The Diels-Alder reactions (Tables I, VI) and sulfone reactions (Tables II, VII) were carried out in 400-ml. pressure bottles at room temperature. The volume of the reaction mixture was calculated from the weight of the components and densities. For the sulfone reaction, solvent, diene and

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[13] W. J. Moore, "Physical Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, p. 528.

[14] For the butadiene-maleic anhydride reaction in benzene the energy of activation is 11.7 kcal.; B. Eisler and A. Wassermann, *J. Chem. Soc.*, 1943 (1953).

[15] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., New York, N. Y., 1941, p. 383.

[16] P. N. Kogerman, *Sitsher. naturforsch.-Ge.. Univ. Tariu*, **41**, No. 3-4, 62 pp. (1934); *C. A.*, **29**, 3297 (1935).

[17] Reference 15, p. 365.

[18] J. F. Norris and D. Rubenstein, THIS JOURNAL, **61**, 1169 (1939).

[19] J. Boeseken and W. J. F. de Rijck van der Gracht, *Rec. trav. chim.*, **56**, 1203 (1937).

TABLE VIII

COMPETITIVE REACTIONS[a]

Expt.	Sulfur dioxide		Solvent		Vapor phase SO_2, mole	Products			
						II		III	
	G.	Mole	G.	Mole		G.	Mole	G.	Mole
In tetrahydrofuran									
22	2.90	0.0453	32.0	0.444	0.0043	7.34	0.0407	0.047	0.00032
23	5.85	.0914	28.3	.393	.0089	7.19	.0398	.101	.00069
24	15.95	.249	23.3	.3235	.0209	6.71	.0372	.374	.00256
25	27.65	.432	14.6	.2025	.0334	6.00	.0332	.942	.00645
In mesitylene									
26	2.75	0.0429	29.9	0.249	0.0057	7.25	0.0402	0.0914	0.000625
27	6.30	.0973	26.7	.222	.0120	7.01	.0388	.1928	.00132
28	14.75	.2300	22.9	.1905	.0239	6.35	.0352	.522	.00358
29	28.75	.449	14.9	.124	.0366	5.64	.0312	1.035	.0071
In benzene									
30	2.80	0.0437	31.2	0.400	0.0044	7.30	0.0405	0.131	0.000898
31	2.90	.0454	30.7	.3955	.0047	7.33	.0407	.1425	.000975
32	5.85	.0914	27.7	.3548	.0091	7.04	.0390	.309	.00211
33	14.05	.2195	24.0	.3075	.0197	6.40	.0355	.676	.00463
34	30.05	.469	14.5	.1858	.0352	5.40	.0299	1.440	.00985
In chloroethyl ether									
35	2.85	0.0445	43.5	0.3040	0.0052	7.17	0.0398	0.163	0.001115
36	5.35	.0836	37.9	.265	.0103	6.94	.0385	.308	.002107
37	14.65	.229	32.1	.224	.0232	6.38	.0354	.789	.00540
38	32.65	.5105	19.6	.1368	.0388	5.32	.0295	1.61	.01101
In chloroform									
39	3.55	0.0554	53.0	0.444	0.0050	7.03	0.0390	0.213	0.00146
40	6.35	.0992	46.9	.392	.0091	6.85	.0380	.403	.00278
41	14.85	.2318	38.8	.325	.0193	6.13	.0340	.930	.00636
42	25.90	.405	25.5	.2135	.0311	5.50	.0305	1.42	.00971
In liquid sulfur dioxide									
43	53.15	0.830	..	....	0.0500	4.40	0.0244	2.37	0.0162

[a] Taken: 3.55 g. (0.0433 mole) of I and 4.25 g. (0.0434 mole) of maleic anhydride.

hydroquinone (0.01 g.) were added in order. Then the gas inlet (a rubber stopper holding two pieces of glass tubing) was attached and the bottle cooled in ice–salt. The longer inlet tube reached almost to the bottom of the bottle, the shorter outlet tube was attached to a drying tube. The outside opening of the inlet tube was closed during cooling. When the bottle was cold, purified sulfur dioxide was passed in. The approximate amount was measured by a rotameter; the exact weight was found by weighing the pressure bottle.

The volume of the solution was calculated from the weight of the components and densities. The quantity of sulfur dioxide in the liquid phase was found by subtracting sulfur dioxide vapor from the sulfur dioxide total. The vapor quantity was calculated for ideal solutions

$$n_v = \frac{nP_0}{n_t(RTK/V + P_0/n_t)} \qquad (7)$$

where

n_v = moles of sulfur dioxide in the vapor phase
P_0 = vapor pressure of sulfur dioxide at $T°$ absolute temperature[20]
n_t = total moles in the vessel
R = gas constant
K = compressibility factor[20]
V = volume of the vapor phase

At the end of the reaction, solvent and volatile reactants were removed *in vacuo*.

Competitive Reactions.—These reactions (Tables III, IV, VIII) were also run in 400-ml. pressure bottles. Maleic anhydride, solvent, hydroquinone (0.01 g.), sulfur dioxide and compound I were added in order. At the end of the reaction volatile components were vacuum distilled and the residue analyzed for II and III.

The Diels–Alder adduct II was measured as *cis*-1,2-dimethyl-1-cyclohexene-4,5-dicarboxylic acid (IV). This is insoluble in water while maleic acid (from excess maleic anhydride) is soluble. In a typical model determination, the sample was dissolved in 10 ml. of 10% sodium hydroxide by boiling. Cooling in ice and adding 4 ml. of concentrated hydrochloric acid precipitated IV. This was filtered, washed three times with 5 ml. of ice cold water. The solid was dissolved in 100 ml. of 50% ethanal, then titrated with 0.25 *N* sodium hydroxide. This analysis was tested on four samples of II; quantities taken and found were: (1) 1.0812 g., 1.075 g.; (2) 1.0284 g., 1.025 g.; (3) 1.2314 g., 1.230 g.; (4) 0.9955 g., 0.990 g.

The sulfone was determined by quantitative dissociation to I and sulfur dioxide and measurement of sulfur dioxide by reaction with excess standard sodium hydroxide, oxidation of sulfite to sulfate, and titration of excess alkali.[5] In a typical model determination, the sample plus 15 ml. of trimethylbenzene was refluxed (160°) for 1.5 hours. Liberated sulfur dioxide was absorbed in 50 ml. 0.25 *N* sodium hydroxide containing 1 ml. of 50% hydrogen peroxide. Excess base was titrated with 0.25 *N* hydrochloric acid. This analysis was tested on four samples of III; quantities taken and found were: (1) 0.4495 g., 0.449 g.; (2) 0.5280 g., 0.529 g.; (3) 0.4855 g., 0.484 g.; (4) 0.5521 g., 0.551 g.

In the competitive reactions approximately 1-g. samples of the product residue were used for the determination of II and 2–5-g. samples for III. The procedure was tested on three known mixtures.

(1) From a solution of 5.302 g. of II, 0.4902 g. of III, 0.5 g. of maleic anhydride and 48 g. chloroform, the solvent was removed *in vacuo* and the residue analyzed; found: 5.25 g. of II and 0.484 g. of III.

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[20] J. W. Mellor (ed.), "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. X, Longmans, Green and Co., New York, N. Y., 1930, pp. 191, 195.

TABLE IX

COMPETITIVE REACTIONS AT 0° AND 50°[a]

Expt.	t, °C.	Sulfur dioxide G.	Sulfur dioxide Mole	Solvent G.	Solvent Mole	Vapor phase SO_2, mole	Products II G.	Products II Mole	Products III G.	Products III Mole
					In chloroform					
44	0	2.70	0.0422	54.05	0.453	0.0017	7.11	0.0395	0.155	0.00106
45	0	2.80	.0437	52.95	.444	.0017	7.13	.0396	.170	.00116
46	50	2.70	.0422	52.60	.4405	.0032	7.22	.0400	.254	.001735
47	50	2.80	.0437	52.75	.442	.0033	7.20	.0399	.247	.00169
					In tetrahydrofuran					
48	0	14.15	0.221	24.1	0.334	0.0072	6.87	0.0382	0.128	0.000875
49	0	14.60	.228	23.65	.328	.0080	6.86	.0381	.133	.000913
50	50	14.35	.224	23.7	.329	.0152	6.82	.0378	.505	.00345
51	50	14.75	.230	23.4	.3245	.0156	6.80	.0377	.510	.00348

[a] Taken: 3.55 g. (0.0433 mole) of I and 4.25 g. (0.0434 mole) of maleic anhydride.

(2) From a solution of 5.140 g. of II, 0.517 g. of III, *ca.* 0.5 g. of maleic anhydride in 28 g. of benzene, the solvent was removed, etc.; found: 5.10 g. of II and 0.511 g. of III.

(3) From a mixture of 4.473 g. of II, 1.004 g. of III, 0.111 g. of polysulfone (a possible by-product), 0.7785 g. of maleic anhydride, and 32 g. of chloroethyl ether, the polysulfone was removed by filtration. The solvent was removed, etc.; found: 4.37 g. of II and 0.966 g. of III.

Before calculating the ratio of rate constants and dielectric constants, sulfur dioxide in the vapor phase was estimated by equation 7, and the amount subtracted from total sulfur dioxide. The dielectric constant D was calculated for ideal solutions

$$D = \Sigma X_i \cdot D_i \qquad (8)$$

where X_i is the mole fraction of the i'th component and D_i is its dielectric constant. The following dielectric constant data were used: I, 2.102 at 25°[21]; maleic anhydride, 50.0 at 60°[22]; sulfur dioxide, 14.3 at 14.5°, 13.3 at 32°,[23] and 13.6 at 27° by interpolation; chloroform, 4.806 at 20°[24]; benzene, 2.284 at 20°[25]; bis-(β-chloroethyl) ether, 21.2 at 20°[26]; tetrahydrofuran, 7.39 at 25°[27]; mesitylene, 2.356 at 20°.[28]

Stability of III.—An approximately one molar aqueous solution of III was refluxed for one hour. No sulfur dioxide was detected in the solution or vapor by litmus paper or odor.

Compound III, 1.1 g., and maleic anhydride, 0.8 g., dissolved in 14.7 g. of tetrahydrofuran, were allowed to stand for 6 weeks at room temperature. The solution was evaporated and the residue dissolved in 15 ml. of 10% sodium hydroxide. Cooling, filtering and washing gave 0.8 g. of III, m.p. 129–131°. When the alkaline filtrate was acidified with hydrochloric acid, no precipitate of IV formed.

In a second experiment, 1.0 g. of III, 4.0 g. of maleic anhydride and 37 ml. of chloroethyl ether were allowed to stand for 6 days at room temperature. The solution was distilled *in vacuo*, the residue was treated with 15 ml. of hot, 10% sodium hydroxide. After cooling and extraction with 50 ml. of benzene, distillation of the benzene gave 1.0 g. of III as the residue, m.p. 131.5–133.5°. The alkaline filtrate gave no precipitate on acidifying.

In a third experiment, 1.0 g. of III, 4.0 g. of maleic anhydride and 37 ml. of benzene were allowed to stand for 6 days at room temperature. Separating this mixture as before gave 0.93 g. of III, m.p. 125–128°, while the alkaline filtrate gave no precipitate on acidifying.

Competitive Reactions at 0° and 50°.—Calculations and experimental procedure were the same as for the room temperature reactions, except that 200-ml. pressure bottles were used at 50 ± 0.5° (Tables V and IX).

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[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

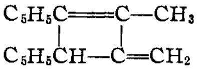
Cyclobutane Diolefins. 1,2-Diphenyldimethylenecyclobutane[1,2]

BY A. T. BLOMQUIST AND YVONNE C. MEINWALD

RECEIVED DECEMBER 3, 1959

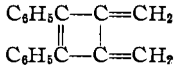
Thermal decomposition of 1,2-bis-(dimethylaminomethyl)-3,4-diphenylcyclobutane dioxide affords a 1:1 mixture of isomeric dienes, 1,2-diphenyldimethylenecyclobutane (III) and 3-methylene-1,4-diphenyl-2-methylcyclobutene (I). The completely exocyclic conjugated diene III undergoes normal 1,4-Diels–Alder addition reactions with both maleic anhydride and tetracyanoethylene.

The unusual formation of spiro compounds *via* 1,2-cycloaddition of tetracyanoethylene (TCNE) to certain conjugated cyclobutane polyolefins, such as I and II, was described in earlier papers.[2a,c] Subsequently, J. K. Williams also observed similar addition reactions for other derivatives of methylenecyclobutane.[3] On the basis of pertinent studies reported to date, the facile 1,2-cycloaddition of TCNE to 1,3-conjugated dienes appears to be limited to dienes which possess a rigid transoid arrangement of the double bonds and hence are



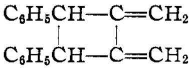
$$\begin{array}{l} C_5H_5C{=\!=\!=}C{-}CH_3 \\ \;\;\;\;\;\;\;\;\;| \qquad\;\; | \\ C_5H_5CH{-}C{=}CH_2 \end{array}$$

I



$$\begin{array}{l} C_6H_5C{-}C{=}CH_2 \\ \;\;\;\;\;\;\;\;\;\| \quad\;\; | \\ C_6H_5C{-}C{=}CH_2 \end{array}$$

II



$$\begin{array}{l} C_6H_5CH{-}C{=}CH_2 \\ \;\;\;\;\;\;\;\;\;\;| \qquad | \\ C_6H_5CH{-}C{=}CH_2 \end{array}$$

III

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[1] This study was supported by the National Science Foundation, Grants NSF-G2922 and NSF-G5923.

[2] For preceding related papers see A. T. Blomquist and Y. C. Meinwald: (a) THIS JOURNAL, **79**, 5316 (1957); (b) **79**, 5317 (1957); (c) **81**, 667 (1959).

[3] J. K. Williams, *ibid.*, **81**, 4013 (1959).