

To the filtrate was added 20 ml. of pentane and the mixture was cooled to 0° to give 1.85 g. (44%) of pyrazoline IV, m.p. 147–149°. This material was identical in every way with the pyrazoline synthesized by reaction of the nitrosourea with lithium ethoxide in diethyl fumarate.³

Thermal Decomposition of N-Nitroso-N-(2,2-diphenylcyclopropyl)-urea in Varying Concentrations of Cyclohexene.—Decompositions were effected in a reaction flask that contained a magnetic stirring bar and was held at 82° by refluxing *t*-butyl alcohol in an outer jacket. Before use, Eastman cyclohexene was distilled from lithium aluminum hydride and Phillips pure grade heptane was distilled through a column packed with metal turnings. Prior to the addition of the solvents, the vessel was brought to temperature and thoroughly flushed with dry nitrogen. The appropriate volumes of cyclohexene and *n*-heptane were pipetted into the reaction vessel to give a total volume (25°) of 50 ml. In calculating the concentration of the cyclohexene, corrections were employed for the change in density of cyclohexene upon heating to 77.6°¹⁴ and the change in density of *n*-heptane upon heating to 80°.¹⁵ To the hot stirred mixture was then added a weighed pellet (*ca.* 1.0 mmole) of the nitrosourea.¹⁵ The reaction was allowed to proceed for 10 min. during which time gas evolution was measured. In general, about 1.5 equivalents of

(14) F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953, pp. 65, 162; J. Timmerman, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Press, New York, N. Y., 1950, pp. 60, 205.

(15) The total yield of spiropentane and 1,1-diphenylallene was found to vary with the batch of nitrosourea. For this reason, all of the runs using solvent mixtures were made from the same initial batch of starting material.

gas was evolved. A mark on the side of the reaction vessel and the absence of refluxing solvent in the condenser in the gas collection line established that the volume of the solvent underwent no significant change during the course of the reaction. At the end of 10 min., the reaction mixture was transferred by a pipet to a 100-ml. volumetric flask. The reaction vessel was rinsed with heptane and the washings were added to the volumetric flask. The solution was then made up to 100 ml. with heptane and stored in the refrigerator.¹⁶

The absolute amount of 1,1-diphenylallene was determined with a Beckman Model DU spectrophotometer employing the absorbance at 250 m μ . The absolute amount of the spiropentane was determined by removing the hydrocarbon solvent from the reaction product and adding a known weight of methyl- α -methyl cinnamate (internal standard) to the residue. Analyses were carried out by g.l.p.c. using a 10-ft. column (1/8 in. inside diameter) packed with 5% by weight of Apiezon L on 60–80 mesh Gas Chrom Z using a column temperature of 230° and a flame ionization detector. Integrated areas were used for the calculations and were compared with standard mixtures of spiropentane and ester. In all cases, the total yield of spiropentane plus allene ranged between 75 and 81%.

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(16) 1,1-Diphenylallene tends to polymerize upon standing.¹⁷ This polymerization is greatly accelerated when the liquid allene is warmed. However, it was found that under our reaction conditions (dilute solution, short heating periods) the allene is stable.

(17) L. Skattebol, *Tetrahedron Letters*, 167 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GEORGIA, ATHENS, GA.]

Organic Peroxides. III. The Behavior of Cyclohexaneformyl Peroxide in the Presence of Excess Stable Radicals. The Simultaneous Determination of Kinetics and Free Radical Efficiencies in the Thermal Decompositions of Free Radical Initiators¹

BY ROBERT C. LAMB² AND JAS. GRADY PACIFICI³

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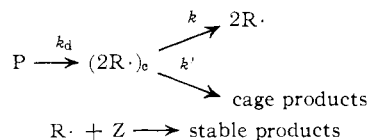
The first-order rate constants and free radical efficiencies in the thermal decompositions of cyclohexaneformyl peroxide in benzene in the temperature range 30–50° were determined spectrophotometrically by measuring the fading of galvinoxyl, which was present in excess. Experiments in which α, γ -bis-(diphenylene)- β -phenylallyl (BDPA) and DPPH were used as scavengers in benzene at 45° gave results similar to those obtained in the galvinoxyl experiments. All of the experiments indicate a low free radical efficiency (24% or less) for the decomposition of cyclohexaneformyl peroxide in benzene. The volatile products formed in the decomposition of cyclohexaneformyl peroxide in benzene containing excess galvinoxyl are ester, acid, bicyclohexyl, cyclohexane, and cyclohexene.⁴ On the basis of the slight dependence of the free radical efficiencies upon temperature, it is argued that these products are formed in cage reactions of radicals, rather than in rearrangement reactions of the peroxide.

Introduction

A new modification of an old method for determining free radical efficiencies was suggested recently.⁵ The method consists of using an excess⁶ of a stable free radical as a scavenger for reactive free radicals formed in the decomposition of an initiator. The use of an excess of scavenger enables one to determine the free

radical efficiency of the initiator and the first-order rate constant of its decomposition in the same experiment.

The (oversimplified)⁷ mechanistic scheme used in this work may be described as



where P = peroxide, $(2R\cdot)_c$ = solvent cage containing a pair of reactive radicals, $R\cdot$ = reactive radical, and Z = stable radical used as scavenger. Assuming the steady state in $R\cdot$ and $(2R\cdot)_c$, one obtains

$$-dZ/dt = 2k_d f P, \text{ where } f = k/(k + k')$$

which may be integrated with proper limits to give the two eq. 1 and 2

$$\ln(Z - Z_\infty)/(Z_0 - Z_\infty) = -k_d t \quad (1)$$

$$f = (Z_0 - Z_\infty)/2P_0 \quad (2)$$

(7) R. M. Noyes, *J. Phys. Chem.*, **65**, 763 (1961), and literature cited therein.

(1) Supported by the Petroleum Research Fund administered by the American Chemical Society, Grant PRF-869-A-4. This paper was read at the Southeastern Regional Meeting of the American Chemical Society in Charlotte, N. C., Nov. 15, 1963. Paper I in this series is given as ref. 5. Paper II: R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963).

(2) To whom correspondence should be addressed.

(3) PRF Predoctoral Fellow, 1962–1963.

(4) It has been reported by Hart and Wyman that the only products of decomposition of cyclohexaneformyl peroxide in carbon tetrachloride at 70° are cyclohexyl chloride and ester. Apparently, the peroxide behaves quite differently in the two solvents; *cf.* H. Hart and D. Wyman, *J. Am. Chem. Soc.*, **81**, 4891 (1959).

(5) R. C. Lamb, F. F. Rogers, Jr., G. C. Dean, Jr., and F. W. Voigt, Jr., *ibid.*, **84**, 2635 (1962).

(6) The word *excess*, as used in this paper, means that enough stable radical is used so that some remains after *all* the initiator has decomposed. In most of the experiments, the ratio of the molar concentrations of stable radical to peroxide (Z_0/P_0) is less than one, inasmuch as the free radical efficiency of cyclohexaneformyl peroxide is low.

TABLE I

THE KINETICS AND FREE RADICAL EFFICIENCIES IN THE DECOMPOSITION OF CYCLOHEXANEFOMYL PEROXIDE IN THE PRESENCE OF EXCESS STABLE RADICALS IN BENZENE

Series no. (no. of expt.)	Radical	$10^4 Z_0^a$	Z_0/P_0 range	$10^4(k_d \pm \text{s.d.})$ min. $^{-1b}$	$t_{1/2}, \text{min.}^c$	f^d	$T, ^\circ\text{C.}$
1 (1)	BDPA	4.80	0.89	Too fast to measure		0.234	85
2 (2)	BDPA	4.80	0.44-0.89	Too fast to measure		.216	75
3 (2)	BDPA	4.80	.44- .89	Too fast to measure		.200	60
4 (3)	BDPA	3.66	.50- .99	30.5 ± 0.3	22.7	.173	45
5 (2)	DPPH	11.23	1.00	35.6 ± 0.9	19.5	.191	44.8
6 (2)	Galv.	143.2	0.49-0.78	Too fast to measure		.191	60
7 (4)	Galv.	143.2	.49- .97	46.8 ± 2.3	14.8	.184	50
8 (5)	Galv.	156.7	.49- .98	31.2 ± 0.7	22.2	.168	45
9 (2) ^e	Galv.	190.6	0.61	$30.8 \pm .9$	22.4	.160	45
10 (4)	Galv.	156.7	0.49-0.98	$18.7 \pm .5$	37.0	.165	40
11 (3)	Galv.	144.4	.52- .87	$15.2 \pm .1$	45.5	.162	38.6
12 (3)	Galv.	156.7	.49- .98	$8.79 \pm .45$	78.8	.161	35
13 (3)	Galv.	138.0	.27- .43	$5.81 \pm .24$	119.3	.135	30

^a Z_0 , the initial molar concentration of stable radical, was the same for all the kinetics runs within a series. Stable radical concentrations were determined spectrophotometrically. In the BDPA experiments, the wave length used was 490 $m\mu$; that used in experiments with DPPH was 518 $m\mu$; and that used in experiments with galvinoxyl was 772 $m\mu$. The extinction coefficients of the three radicals at these wave lengths were 26,289, 12,218, and 607.¹⁰ ^b First-order rate constants, k_d , were determined by least-squares adjustment of data to eq. 1. All runs were followed through 85% reaction. The number of spectrophotometric determinations within each run varied from 6 to 13, excluding the necessary determinations at $t = \infty$. The average value of k_d is given for each series, along with the error between experiments (not intraexperimental precision). The average standard deviation in k_d within individual experiments was $\pm 3\%$. ^c Average half-life in min. ^d f = average efficiency. The average error in efficiencies within series was ± 0.006 . These errors appear to have been random, *i.e.*, efficiencies did not change in a regular fashion with changing Z_0/P_0 . ^e The kinetics samples used in these runs contained added cyclohexanecarboxylic acid at $10^4(\text{HA}) = 5.9$ and 19.8 M .

A system of this type places rather strict requirements on the behavior of its components. Ideally, none of the components (solvent, initiator, stable radical, products) should react with another component, nor should any component other than initiator undergo spontaneous decomposition. Also, if a spectrophotometric method of analysis for Z is used, the reaction products should not absorb at the wave length used for the analysis. If products do absorb, a high value of Z_∞ , hence a low value of the efficiency (f), results (eq. 2, above).

It is therefore obvious that the systems used in such experiments must be chosen carefully. Galvinoxyl^{8,9} is known to be an excellent scavenger for reactive radicals¹⁰ and is also known to be relatively stable at low temperatures in benzene.^{11,12} We have found that galvinoxyl is stable in benzene up to 60 $^\circ$, when the latter has been freshly distilled and vigorously flushed with carbon dioxide. α, γ -Bis-(diphenylene)- β -phenylallyl¹³ (henceforth called BDPA in this paper) is stable in the same medium at temperatures up to 85 $^\circ$. Inasmuch as cyclohexanefomyl peroxide decomposes at a substantial rate at low temperatures,⁴ a series of experiments was conducted with this peroxide to determine the feasibility of using these two radicals and DPPH in experiments of this type. Galvinoxyl was used in the majority of the experiments.

Most of the kinetics runs reported here in which the rates were determined by measuring the fading of the stable radical at the wave length of one of its absorption bands in the visible were performed as follows: Each sample containing the stable radical and the peroxide was degassed and sealed in a 1-cm. square Pyrex tube which served both as kinetics vial and cuvette for the spectrophotometer; thus each kinetics run involved only one sample vial. The run was conducted at reactant concentrations such that the absorbance due to the radical fell in the measurable range. For each temperature, control samples, con-

taining stable radical at the same concentration as used in the kinetics vial (but *no* peroxide), were found to undergo no fading whatever during the period required to complete the reaction.

In one experiment (expt. 17, Table II), higher reactant concentrations were used, which necessitated the use of several samples, each of which, after its heating period, was broken and an aliquot portion of its contents was diluted sufficiently with solvent so that the absorbance due to the stable radical could be measured.

Results and Discussion

The results of 29 kinetics runs on the decomposition of cyclohexanefomyl peroxide, listed in order of increasing stable radical concentration, are summarized in Table I. The rate constants and efficiencies given for each temperature are, for the most part, average values obtained in two or more runs.

TABLE II
VALIDATION EXPERIMENTS: DECOMPOSITION OF CYCLOHEXANEFOMYL PEROXIDE IN BENZENE

Run	Z_0, M	P_0, M	$10^4 k_d \pm \text{s.d.}$ min. $^{-1}$	$t_{1/2}, \text{min.}$	$T, ^\circ\text{C.}$
14 (IR) ^a	0.04	0.04	31.7 ± 2.1	21.9	45.3
15 (IR) ^a	0	.04	12.8 ± 1.7	54.3	38.6
16 ^b	0	.08	5.96 ± 0.06	116.3	30.0
17 ^c	0.04	.08	39.4 ± 1.5	17.6	45.0

^a Infrared band of the carbonyl group in the peroxide at 1766 cm.^{-1} used for analysis. ^b Rate determined by iodometric assay. ^c Samples diluted by a factor of 25, and the 772- $m\mu$ galvinoxyl band used for analysis. The efficiency obtained in this experiment was 0.156.

The rate constants obtained at each temperature are fairly reproducible and do not change with a definite trend when the ratio of initial concentrations of stable radical to peroxide (Z_0/P_0) is changed. This, along with the fact that eq. 1 is obeyed with fair accuracy in each run through about three half-lives, is strong evidence that the reaction is zero order in the stable radical, *i.e.*, there is no significant second-order reaction between the peroxide and the stable radicals under the conditions used. Also, since the efficiencies do not change with any definite trend with increasing Z_0/P_0 ,

(8) G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957).(9) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).(10) P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962).(11) F. D. Greene, W. Adam, and J. E. Cantrill, *ibid.*, **83**, 3461 (1961).(12) P. D. Bartlett, B. A. Gontarev, and H. Sakurai, *ibid.*, **84**, 3101 (1962).(13) C. F. Koelsch, *ibid.*, **79**, 4439 (1957); **84**, 4744 (1932).

the stable radicals must scavenge essentially all of the reactive radicals which escape cage reactions.

The results of the BDPA experiments (at 45°) agree extremely well with those performed with galvinoxyl, especially when it is considered that the initial stable radical concentration (Z_0) is greater by a factor of 43 in the galvinoxyl experiments (series 4, 8, and 9, Table I). The results of the two runs with DPPH (series 5) are not significantly different from those obtained with galvinoxyl and BDPA when one takes into consideration the high rate of peroxide decomposition which is being measured by the method used.

Some of our early products study work seemed to indicate that a rather large yield of cyclohexanecarboxylic acid (0.4 mole/mole of peroxide) is obtained when cyclohexaneformyl peroxide is decomposed in the presence of excess galvinoxyl. More recent work has caused us to revise the yield drastically downward (see Table III), but in the interim the effect of added cyclohexanecarboxylic acid on the rate and efficiency in the decomposition of the peroxide was investigated.¹⁴ No effect could be detected under the conditions used (compare series 8 and 9, Table I).

TABLE III
SOME PRODUCTS OF THE DECOMPOSITION OF
CYCLOHEXANEFORMYL PEROXIDE IN BENZENE CONTAINING
EXCESS GALVINOXYL^a

Product	Yield (mole/mole peroxide)	Yield (equiv. C-6 groups/mole peroxide)
Cyclohexanecarboxylic acid	0.12	0.12
Cyclohexyl cyclohexanecarboxylate	.40	.80
Bicyclohexyl	.04	.08
Cyclohexene	.28	.28
Cyclohexane	.07	.07
Radical yield	...	2f = 0.34 ^b
	Total	1.69 ^c

^a $Z_0 = 0.06 M$; $P_0 = 0.12 M$. ^b Taken from the experiments at 45° in Table II. ^c This is equivalent to 84.5% of the C-6 groups.

The rates of decomposition obtained by measuring the rates of fading of excess stable radicals in benzene (Table I) have been validated by independent measurement (Table II). The rate was determined by measuring the disappearance of the peroxide carbonyl band, both in the presence and absence of galvinoxyl (runs 14 and 15), and, in addition, the rate was measured by iodometric titration (run 16). Of these, the poorest agreement is found in run 15, in which the half-life obtained (54.3 min.) at 38.6° differs by 20% from the average half-life obtained (45.5 min.) by measuring the fading of galvinoxyl (series 11, Table I). In Table II, we have also reported the results of an experiment in which the rate was determined by measuring the fading of galvinoxyl, but in which both Z_0 and P_0 are considerably greater than were used in the experiments in Table I (run 17 in Table II). The observed rate is 21% greater than the average rate obtained at 45° at lower concentrations (series 4, 8, and 9 in Table I), and it is also greater than the rate measured by infrared analysis at nearly the same reactant concentrations (run 14, Table II). The reason for the discrepancy is not clear, but it cannot be ascribed to a direct reaction between galvinoxyl and the peroxide at higher reactant concentrations, for such a reaction would destroy more galvinoxyl per mole of peroxide than would be destroyed in the reaction at lower Z_0 and P_0 . Thus a direct reaction between galvinoxyl and peroxide would increase both the rate and the apparent efficiency, yet the efficiency obtained in run 17

in Table II is only 0.156, somewhat lower than the average value obtained at the same temperature using lower reactant concentrations.

The experiments involving cyclohexaneformyl peroxide and stable radicals in benzene are all essentially in agreement, both in respect to rates and free radical efficiencies, although the reactant concentrations are varied over a thousandfold range; and, at given levels of Z_0 and P_0 , the ratio Z_0/P_0 is varied in some cases by a factor of two. The data are therefore valid, even if, in some cases, the experimental accuracy is not superb.

A plot of $\log k_a/T$ vs. $1/T$ using the data in Table I shows a slightly S-shaped curve about the least-squares line. The parameters obtained are $\Delta H^* = 20.2 \pm 0.5$ kcal. and $\Delta S^* = -10.5$ e.u. Although this high negative value of ΔS^* would not be in disagreement with a mechanism of peroxide decomposition in benzene involving rearrangements which proceed through cyclic transition states, other considerations lead us to doubt, if not entirely reject, such a mechanism.

The main consideration which suggests a purely radical mechanism for the decomposition in benzene concerns the slight temperature dependence of the free radical efficiencies. The expression $f = k/(k + k')$ can be rearranged to give $k/k' = f/(1 - f)$. Combining this result with the transition state equation leads to eq. 3

$$\log f/(1 - f) = -\frac{(\Delta H_d^* - \Delta H_c^*)}{2.303R} \frac{1}{T} + \frac{(\Delta S_d^* - \Delta S_c^*)}{2.303R} \quad (3)$$

where $\Delta H_d^* - \Delta H_c^* = E_a^d - E_a^c$ is the difference between the enthalpies or energies of activation of the diffusion of radicals from the solvent cage and the reaction of radicals with each other therein, and the intercept of the equation gives the difference in the activation entropies of the two processes. Least-squares adjustment of efficiencies obtained with BDPA and galvinoxyl in Table I to eq. 3 gives the values $E_a^d - E_a^c = 2.3 \pm 0.2$ kcal. and $\Delta S_d^* - \Delta S_c^* = +4.2 \pm 0.7$ e.u.

Herk, Feld, and Szwarc have treated data analogously using a quite different system.¹⁵ It was found that in the photolysis of azomethane in isooctane between 6–95° the only products are methane, ethane, and nitrogen, and all the ethane is formed in the cage reaction of methyl radicals. The yield of methyl radicals per mole of azomethane decomposed is given by the quantity CH_4/N_2 . In terms of the semantics used in this paper, $f = \text{CH}_4/2\text{N}_2$, since the theoretical yield of methyl radicals from azomethane is 2 moles/mole of reactant. It follows that $f/(1 - f) = (\text{CH}_4/\text{N}_2)/(2 - \text{CH}_4/\text{N}_2)$. Using the data obtained in the most accurate series of experiments, Herk, Feld, and Szwarc plotted the logarithm of the latter value vs. $1/T$ and obtained $E_a^d - E_a^c = 2$ kcal.; since $E_a^c = 0$ for the cage recombination of methyl radicals, it follows that 2 kcal. is an estimate of the activation energy for diffusion of methyl radicals from the solvent cage in isooctane. We have recalculated this value somewhat more precisely from their data determined in the series of experiments using 3600-Å. light, and obtained $E_a^d - E_a^c = 2.17 \pm 0.14$ kcal., and $\Delta S_d^* - \Delta S_c^* = +4.9 \pm 0.4$ e.u.¹⁶

Herk, Feld, and Szwarc called attention to the similarity in the value of $E_a^d - E_a^c = 2.2$ kcal., and the activation energy obtained from the temperature coefficient of the viscosity of isooctane, 2.1 kcal. Similarly, for the decomposition of cyclohexaneformyl peroxide

(15) L. Herk, M. Feld, and M. Szwarc, *ibid.*, **83**, 2998 (1961).

(16) It is not surprising that this difference in activation entropies is positive, both for the decomposition of cyclohexaneformyl peroxide and for azomethane. It is probable that ΔS_d^* will be positive for any initiator, and ΔS_c^* should always be negative; hence the difference must be positive.

(14) H. Hart and R. A. Cipriani, *J. Am. Chem. Soc.*, **84**, 3697 (1962).

in benzene, our value for the quantity $E_a^d - E_a^c = 2.3 \pm 0.2$ kcal., is identical with the activation energy obtained from the temperature coefficient of the viscosity of benzene, 2.4 kcal.¹⁷ Here, then, are two quite different initiator systems in which the free radical efficiencies increase with decreasing solvent viscosity in quite an analogous way. Since it is certain that the photolysis of azomethane proceeds by a free radical path only (that is, there is no rearrangement giving ethane), the similarity in the behavior of the two systems suggests that the decomposition of cyclohexaneformyl peroxide in benzene is probably free of rearrangement reactions.

The hypothesis developed here is fundamentally the same as that of DeTar and Weis, who have argued convincingly that in the decomposition of δ -phenylvaleryl peroxide in carbon tetrachloride, the slight dependence of product yields upon temperature indicates that the decomposition is probably all homolytic.¹⁸ In that system, the free radical efficiency is half the yield of δ -phenylbutyl chloride. From the average values of the latter obtained at 55 and 77°, one may calculate $E_a^d - E_a^c = 2.1$ kcal., and $\Delta S_a^* - \Delta S_c^* = +5.5$ e.u.; the difference in E_a 's should be compared with a value of 2.8 kcal. obtained from the temperature coefficient of the viscosity of carbon tetrachloride.

The absence of rearrangement reactions in the cyclohexaneformyl peroxide-benzene system has not, of course, been proved. The point being made is that unless $\log f/(1-f)$ in any such system shows significantly more temperature dependence than $\log 1/\eta$ for the solvent, the homolysis mechanism should suffice in the absence of convincing independent evidence to the contrary.

The products study (Table III) is not as quantitative as one would like; 84.5% of the C-6 groups have been accounted for, when the 2f free radicals which become attached to galvinoxyl during the decomposition are added to the yields of volatile products. Apparently, the four usual cage reactions are operative: (a) recombination and disproportionation of acyloxy and alkyl radicals, forming ester, acid, and cyclohexene; and (b) recombination and disproportionation reactions of alkyl radicals forming dimer, cyclohexane, and cyclohexene. The most important of these is the recombination of acyloxy radicals with alkyl radicals, since ester is the predominant product. It is probable that the average activation energy for these cage reactions is near zero.

Finally, it should be remarked that kinetics experiments of the type described here have been attempted with several systems, using, in most cases, benzene as the solvent. Experiments with the remarkably stable red liquid radical, di-*t*-butyl nitroxide,¹⁹ gave unrealistically high rates in the decompositions of cyclohexaneformyl peroxide in benzene at 45°, and in the decomposition of 6-heptenoyl peroxide at 77° in toluene. BDPA is also very stable in benzene at higher temperatures, and has been applied successfully to the decompositions of a series of *p*-substituted γ -benzylidenebutyryl peroxides in benzene in the 50–70° range.²⁰ Galvinoxyl apparently undergoes some spontaneous decomposition in benzene at 60° and above when heated for several hours. The runs in series 6 in Table I were possible because the half-life of the per-

oxide at 60° is less than 5 min.; the reaction was thus complete in 45 min., during which time no fading could be detected in the control sample.

Experimental²¹

Galvinoxyl was prepared by the method of Coppinger,⁸ and purification was accomplished by the method described by Bartlett and Funahashi,¹⁰ except that our final recrystallization was from ethanol rather than carbon tetrachloride.

BDPA was prepared by methods described by Koelsch,¹³ using the modification described by Solar and Lindquist for the preparation of α, γ -bis-(diphenylene)- β -phenylallyl alcohol.²²

Cyclohexaneformyl peroxide was prepared by adding the acid chloride to a slight excess of sodium peroxide in an ice-water-ether slurry. The peroxide was recrystallized twice from methanol; the methanol was removed each time by decantation. Finally, benzene portions were added, then subsequently removed by evacuation in order to remove the last traces of methanol.

Although this peroxide is obtained in well defined crystals when recrystallized from methanol (using a Dry Ice-acetone bath), the peroxide decomposes rapidly in the melt at room temperature. Therefore, as soon as the methanol was removed, the peroxide was dissolved in benzene, and the concentrated solution was frozen and stored at -70°.

Kinetics Runs.—The benzene used in the kinetics experiments was of reagent grade, and was freshly distilled just prior to use. After distillation, the benzene was flushed vigorously with carbon dioxide by immersing a carbon dioxide inlet under the surface of the benzene. The gas flow rate was adjusted so as to cause vigorous agitation of the benzene. The benzene was flushed thusly for about 5 min.

The peroxide stock solution was prepared from the concentrated solution described above. The initial peroxide concentration was determined by iodometric titration of three aliquots of the peroxide stock solution.

A stock solution of the stable radical in benzene was then prepared, and aliquots of the two stock solutions were mixed as desired, then sufficient benzene was added to give an initial absorbance due to the stable radical which fell in a desirable range.

Kinetics vials were prepared from 1-cm. square Pyrex tubing.²³ Each vial was equipped with a flat bottom, and was connected at the top to a 10/30 $\frac{1}{8}$ male joint. The circular tube leading to the joint was previously constricted. The vials were filled through the constriction with the kinetics sample with the aid of a hypodermic syringe equipped with a long needle. The vials were then attached to a vacuum manifold. The contents of the vials were then frozen, the system was degassed, the solution was melted, the system was flushed with carbon dioxide, and the cycle was repeated. The vials were then sealed off under vacuum at the previously prepared constriction.

The vials were wrapped with aluminum foil prior to degassing. The wrapping remained on the vials during the course of the kinetics run, except during spectrophotometric analysis.

The bath temperatures were controlled to 0.02°; temperatures were measured with 0.1° NBS standardized thermometers. In order to take readings, the vials were removed from the bath at intervals and cooled with ice water to 0°; the bath oil was removed with organic solvents and the spectrophotometric reading taken. The vial was wrapped again with foil and returned to the bath as soon as possible.

Kinetics runs in which infrared or iodometric analyses were used were performed by standard methods. Isopropyl alcohol was used as titration solvent in the iodometric runs.

Product Analyses.—Products were analyzed by v.p.c. methods completely analogous to those used for the decompositions of 6-heptenoyl peroxide in toluene described in paper II in this series.¹ Column A was used for the analysis of cyclohexane and cyclohexene; column B was used for bicyclohexyl and ester. The cyclohexanecarboxylic acid was extracted from a decomposition mixture with dilute sodium bicarbonate and, after isolation, it was estimated by titration with standard sodium hydroxide solution.

Acknowledgment.—We are indebted to the Petroleum Research Fund for support; to the University of

(17) A. Weissberger, Ed., "Organic Solvents, Vol. VII, Technique of Organic Chemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., p. 24.

(18) D. F. DeTar and C. Weis, *J. Am. Chem. Soc.*, **79**, 3041 (1957).

(19) A. K. Hoffman and A. T. Henderson, *ibid.*, **83**, 4671 (1961).

(20) Unpublished work, Ph.D. Dissertation, Leonard P. Spadafino, August, 1963.

(21) A line-operated Beckman Model DU spectrophotometer, equipped with a specially built box-like cover for the cell chamber, was used for measuring stable radical concentrations spectrophotometrically. A Perkin-Elmer Model 421 infrared spectrophotometer was used in kinetics runs determined by infrared analysis (Table II). A Beckman GC-2 gas chromatograph was used in the products study (Table III).

(22) S. L. Solar and R. M. Lindquist, *J. Am. Chem. Soc.*, **82**, 4285 (1960).

(23) This tubing, obtained from the Fischer and Porter Co., Warminster, Pa., had two opposite sides frosted; the other two sides were polished.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF NORTH DAKOTA, GRAND FORKS, N. D.]

Chemistry of Ylids. X. Diphenylsulfonium Alkylides—A Stereoselective Synthesis of Epoxides¹

By A. WILLIAM JOHNSON, VICTOR J. HRUBY, AND JOSEPH L. WILLIAMS

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The preparation and properties of diphenylsulfonium benzylide (8) and butylide (9) are described. Both ylids can be dissociated into carbenes and phenyl sulfide. The benzylide 8 reacts stereoselectively with benzaldehydes to form *trans*-stilbene oxides.

Introduction

From a study of the properties of phosphorus ylids² it became obvious that ylids containing heteroatoms other than phosphorus should be capable of existence. The major requirement appeared to be the ability of the heteroatom to stabilize the ylid carbanion, usually by overlap of the free electron pair with the vacant, low-energy d-orbitals of the heteroatom. In instances where this was not possible, such as many nitrogen ylids,³ the substances were capable of only fleeting existence. At an early date Ingold and Jessop,⁴ although apparently not using this line of reasoning, prepared a sulfur ylid, 9-dimethylsulfonium fluorenylide (1). In more recent years Johnson^{5a} and Wittig^{5b} have investigated the chemistry of ylids containing group V heteroatoms other than phosphorus.

Some time ago we undertook to investigate the physical and chemical properties of several new ylids and chose first to examine the chemistry of sulfonium ylids. We were particularly anxious to determine how these ylids would react with carbonyl compounds under the conditions of the well-known Wittig reaction.⁶ Since all ylids are nucleophiles, albeit of varying strength, we expected they would undergo at least the first step of the Wittig reaction, *i.e.* the attack of the ylid carbanion on the carbonyl carbon to form a betaine intermediate (*e.g.*, 2). Whether or not the betaine would dissociate into an olefin (*e.g.*, 3) and an oxide of the heteroatom group (*e.g.*, 4) was expected to depend on the bond energies involved.

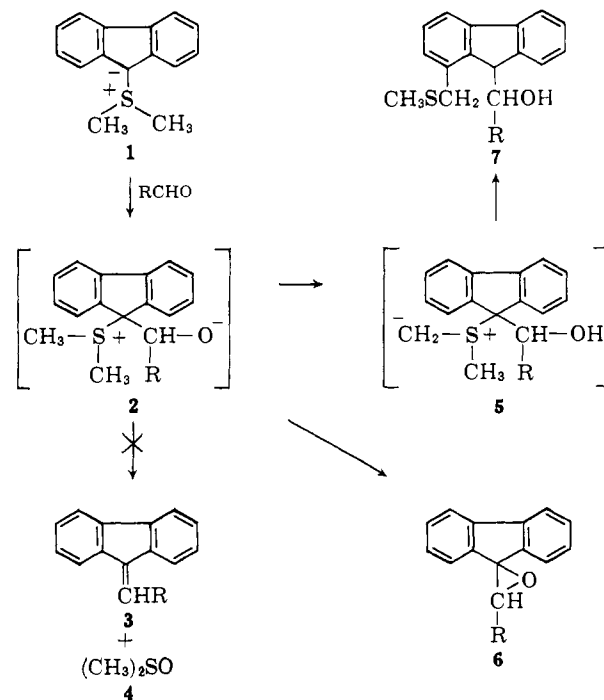
In our original work on the chemistry of sulfonium ylids⁷ we showed that 9-dimethylsulfonium fluorenylide (1) reacted with benzaldehydes to form a mixture of the benzalfluorene oxide (6, R = C₆H₄X) and a rearranged alcohol (7, R = C₆H₄X). The mechanism shown in Chart I was tentatively proposed to account for the observed products. This mechanism was based on the relative carbonyl reactivity sequence, analogy with other sulfonium salt displacements, and

the analogy with the known Sommelet rearrangement of the original ylid 1. Epoxide formation, rather than olefin formation as in the Wittig reaction, was not completely unexpected on the basis of the difference in bond dissociation energies of dimethyl sulfoxide (89 kcal./mole)^{8a} and triphenylphosphine oxide (128 kcal./mole)^{8b} and the known reluctance of hydroxide to attack trivalent sulfur but not tetravalent phosphorus.⁹

On the basis of this work we predicted that most, if not all, sulfonium ylids would form epoxides upon reaction with aldehydes and ketones. This expectation has been verified in the much later work reported by Corey, *et al.*, with dimethylsulfoxonium methylide^{10a} and dimethylsulfonium methylide^{10b} and the more recent reports by Franzen and co-workers using phenylmethylsulfonium methylide.^{10c}

To develop our original reaction between sulfonium ylids and carbonyl compounds into one of practical value for the synthesis of epoxides, two modifications would be required. First, the reactivity of the ylids would have to be increased since the fluorenylide (1)

CHART I



(1) (a) For paper IX in this series see A. W. Johnson, *Chem. Ind. (London)*, 1119 (1963). (b) Taken in part from the thesis of Victor J. Hruby presented to the Graduate School of the University of North Dakota in partial fulfillment of the requirements for the degree of Master of Science, August, 1962. (c) Part of this work was originally presented at the 142nd National Meeting of the American Chemical Society, Division of Organic Chemistry, Atlantic City, N. J., September 10, 1962. Another portion was announced in a preliminary communication, *J. Am. Chem. Soc.*, **84**, 3586 (1962). (d) We gratefully acknowledge the financial support of the National Science Foundation (Grants No. G-17345 and GP-1321).

(2) A. W. Johnson and R. B. LaCount, *Tetrahedron*, **9**, 130 (1960).

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(4) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 713 (1930).

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(7) A. W. Johnson and R. B. LaCount, *Chem. Ind. (London)*, 1440 (1958); *J. Am. Chem. Soc.*, **83**, 417 (1961).

(8) (a) H. Mackle, *Tetrahedron*, **19**, 1159 (1963); (b) A. F. Bedford and C. T. Mortimer, *J. Chem. Soc.*, 1622 (1960).

(9) C. K. Ingold, *et al.*, *ibid.*, 531, 533 (1933).

(10) (a) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962); (b) *ibid.*, **84**, 3782 (1962); (c) V. Franzen and H. E. Driessen, *Tetrahedron Letters*, 661 (1962); *Chem. Ber.*, **96**, 1881 (1963).