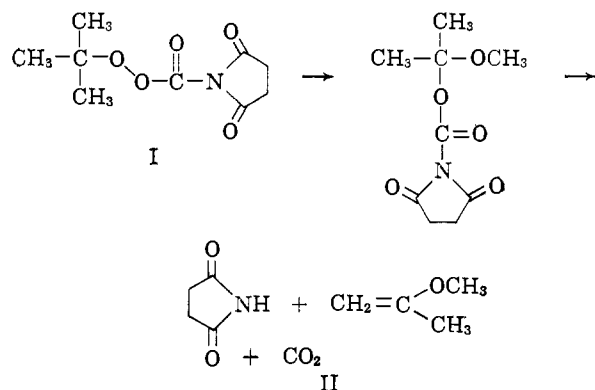


ysis and suggest the lack of high stability for the succinimidyl radical.⁶



Moreover, the products in chlorobenzene at kinetic concentrations and conditions, which were acetone (39%), dimethyl ketal of acetone (25%), isopropenyl methyl ether (35%), carbon dioxide ($\geq 99\%$), and succinimide ($\geq 95\%$), strongly suggest that the predominant mode of decomposition of I in chlorobenzene involves heterolysis of the peroxide bond and concurrent migration of methyl to electron-deficient oxygen (Criegee rearrangement).⁷

For example, isopropenyl methyl ether (II) is most logically accounted for in terms of the scheme given above, while the dimethyl ketal is probably obtained by the reaction of the enol ether with water (giving acetone and methanol) and subsequent reaction of the evolved methanol with more enol ether. The balance of the acetone (14%) may be derived from homolytic fission to give the *t*-butoxy radical, which fragments. The quantitative yield of carbon dioxide and succinimide is also consistent with the known instability of carbamic acids.⁸ Furthermore, when I is decomposed in chlorobenzene containing 2 molar and 15 molar excesses of styrene the carbon dioxide yield decreases by 10% indicating only *ca.* 10% homolytic decomposition. This is in good qualitative agreement with the radical efficiencies determined by Koenig⁹ using galvinoxyl. In contrast, the products from the other percarbamates were consistent with a free radical decomposition. Consequently, the relative rate of homolysis of *t*-butyl *N*-succinimidepercarboxylate (I) is *ca.* one-tenth that indicated in the above rate sequence, and thus this perester appears to be more stable than *t*-butyl percarbamate toward homolysis.

Despite the preference for heterolysis under non-irradiating conditions we have been able to induce homolysis of *t*-butyl *N*-succinimidepercarboxylate (I) photochemically. When a 0.07 *M* solution of the perester in cumene was irradiated with a Hanovia lamp through a Vycor filter for 36 hr. at room temperature, the products obtained were *t*-butyl alcohol (92%), acetone (3%), bicumyl (29%), and succinimide (71%). The

(6) A more quantitative appraisal of the correlation between radical stability and percarbamate homolysis must await further investigation.

(7) (a) R. Criegee, *Ann.*, **560**, 127 (1948); (b) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **83**, 856 (1961); (c) E. Hedaya and S. Winstein, *Tetrahedron Letters*, No. **13**, 563 (1962); (d) E. Hedaya, Ph.D. Dissertation, University of California at Los Angeles, 1962.

(8) (a) M. Frankel and E. Katchalski, *J. Am. Chem. Soc.*, **65**, 1670 (1943); (b) E. Katchalski, C. B. Klubanski, and A. Berger, *ibid.*, **73**, 1829 (1951).

(9) T. Koenig, private communication. We thank Dr. Koenig for making his results known to us prior to publication.

remainder of the product derived from the succinimide fragment of the perester appears to be cumyl *N*-succinimidecarboxylate on the basis of degradation by hydrazinolysis. In comparison thermal decomposition at 110° in cumene yields *t*-butyl alcohol (17%), bicumyl (20%), acetone and its dimethyl ketal (10%), isopropenyl methyl ether ($\geq 50\%$), and succinimide ($\geq 95\%$). The products in the photochemical process are best interpreted in terms of homolysis giving *t*-butoxy and *N*-carboxysuccinimidyl radicals which conceivably could decarboxylate. However, the substantial yield of cumyl *N*-succinimidecarboxylate may reflect the high stability of this intermediate compared to the succinimidyl radical and carbon dioxide. Conditions are being sought where products unambiguously derived from the succinimidyl radical or its acyl isocyanate rearrangement product^{1a,10} can be obtained. Also, other sources of this elusive radical are being examined.¹¹

These results and those obtained in our previous work on *N,N'*-bisuccinimide² strongly imply that the succinimidyl radical is highly unstable with respect to the dimer, succinimide, or even *N*-bromosuccinimide (NBS). Simple molecular orbital calculations suggest that a highly developed π -electron system involving the lone pair on nitrogen and the adjacent carbonyl groups exist in both the ground state molecule and in the radical, and that, consequently, no net stabilization of the radical is realized.² In contrast, conjugation of the free electron occurs in the anilino radical, while conjugation of the electron pair occurs in the ground state molecule, leading to net stabilization of the former. This difference between the anilino and succinimidyl radicals primarily results from the differences in electronegativities of carbon, nitrogen, and oxygen and the assumption of planarity in the ground state molecule. Further experiments on other amino radicals and conjugated free radicals in general are being carried out to test and elaborate this rationalization.

Acknowledgment.—The authors thank Dr. V. Schomaker and Professor C. Walling for helpful discussions.

(10) (a) J. C. Martin and P. D. Bartlett, *J. Am. Chem. Soc.*, **79**, 2533 (1957); (b) H. W. Johnson, Jr., and D. E. Bublitz, *ibid.*, **80**, 3150 (1958); no acyl isocyanate has been detected in our work.

(11) One interesting possibility is *N*-iodosuccinimide, which when irradiated with ultraviolet light through Vycor in benzene solution gives iodine ($\geq 95\%$), *N*-phenylsuccinimide (27%), and succinimide (25%).

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The Thermal Decomposition of *t*-Butyl 2,5-Dioxo-1-pyrrolidineperformate

Sir:

Convincing evidence has recently appeared which indicates that succinimidyl radicals are not the chain carrying species in the *N*-bromosuccinimide brominations of aralkyl¹ and alkyl² hydrocarbons. Preliminary experiments, also recently reported,³ indicate

(1) J. C. Martin and R. E. Pearson, *J. Am. Chem. Soc.*, **85**, 3142 (1963); C. Walling, A. L. Reiger, and D. D. Tanner, *ibid.*, **85**, 3129 (1963); G. A. Russell and K. M. Desmond, *ibid.*, **85**, 3149 (1963).

(2) P. S. Skell, D. L. Tuleen, and P. D. Read, *ibid.*, **85**, 2850 (1963).

(3) E. Hedaya, R. L. Hinman, and S. Theodoropoulos, *ibid.*, **85**, 3052 (1963).

TABLE I
 RATES^a OF DECOMPOSITION OF I AT 100°

Solvent	$k_{IR}^b \times 10^5 \text{ sec.}^{-1}$	Rel. k_{IR}	$k_G^c \times 10^5 \text{ sec.}^{-1}$	n^d	$k_r^e \times 10^5 \text{ sec.}^{-1}$
Cyclohexane			1.10	1.56	0.86
Cyclohexene	0.90	1.00			
Benzene ^f	3.79 ^g	4.21	2.42 ^h	0.39	0.47
Chlorobenzene ^f	4.91	5.34	2.72	0.30	0.40
Nitrobenzene ^f	34.1	38.0	15	0.06	0.45
Acetonitrile	99.0	110			
Methanol	600	670			

^a By least squares. ^b Infrared rate constants determined at 0.1 *M* initial concentration of perester. ^c Pseudo-first-order galvinoxyl rate constants determined at *ca.* 10^{-3} *M* perester and galvinoxyl concentrations. ^d Moles of galvinoxyl decolorized per mole of perester I, *i.e.*, $2 \times \%$ radical/100. ^e Rate of radical formation, *i.e.*, $n/2 \times k_G$. ^f 2 *M* styrene present. ^g Temperature studies give $\Delta H^* = 27.1 \pm 0.3$ kcal./mole, $\Delta S^* = -6.1 \pm 1.0$ e.u. ^h Temperature studies give $\Delta H^* = 29.1 \pm 0.6$ kcal./mole, $\Delta S^* = -2.2 \pm 1.6$ e.u.

results of these kinetic studies are summarized in Table I.

The rate constants obtained by the pseudo-first-order disappearance of scavenger are in reasonable agreement with the infrared results considering the difference in concentration. The over-all change in scavenger absorbance from zero to infinite reaction times can be used to estimate the moles of scavangeable radicals produced and thus the rate of radical formation ($n/2 \times k_G$). The latter rate constants (k_r) are not strongly solvent dependent while over-all rate constants (k_{IR} or k_G) increase with increasing polarity of the medium. These observations are consistent with a dual mechanism for the decomposition of I involving two rate-determining transition states leading individually to both radical and ionic intermediates.

Product studies in all solvents, with the exception of cyclohexene, revealed quantitative formation of suc-

 TABLE II
 VOLATILE AND GASEOUS PRODUCTS^a FROM DECOMPOSITION OF 0.2 *M* SOLUTIONS OF I AT 115°

Solvent	Product, moles/mole of I					
	CO ₂	CH ₄	CH ₃ COCH ₃	<i>t</i> -C ₄ H ₉ OH	CH ₂ =C< OCH ₃ CH ₃	Other
Cyclohexene	0.52	0.01	0.05	0.72	0.24	0.60 ^b
Benzene ^c	0.94	0.04	0.06	0.21	0.58	
Benzene			0.24		0.74	0.12 ^d
Chlorobenzene	0.98	0.01	0.20	0.04	0.70	0.08 ^e
Chlorobenzene ^f	0.85					

^a The gaseous products were quantitatively determined by a volumetric method¹² and identified by their mass spectra. The liquid products were identified and their yields determined quantitatively by n.m.r. and infrared and by g.l.c. ^b Bicyclohexenyl. ^c Containing 30% cyclohexane. ^d Toluene. ^e *o*- and *p*-chlorotoluenes, 2:1 by g.l.c. ^f Initial perester concentration 0.02 *M*, galvinoxyl concentration 0.1 *M*.

that N,N'-bisuccinimidyl is stable and shows no apparent tendency to dissociate to succinimidyl radicals with either thermal or photochemical excitation.

The rates of decomposition of a number of *t*-butyl peresters including *t*-butyl perphenylacetates are sensitive to resonance stabilization of the decarboxylated radicals.⁴ It has been proposed⁵ that the instability of *t*-butyl *N*-arylpercarbamates is similarly due to resonance stabilization of the anilo radicals. We now wish to report the results of our studies of the thermal decomposition of *t*-butyl 2,5-dioxo-1-pyrrolidineperformate (I) which were initiated in the hope of generating succinimidyl radicals.

The perester (I, m.p. 101–102°)⁶ is formed from the reaction of sodium succinimide and *t*-butyl chloroformate. The rates of decomposition of I were measured in several solvents by following the decrease in the perester infrared absorption at 1834 cm.⁻¹ and by pseudo-first-order⁷ disappearance of galvinoxyl⁸ through its visible absorption of 575 m μ . The kinetic data obtained by both methods gave first-order rate plots which were linear for three half-lives.⁹ The

cinimide as a decomposition product. The results of our studies on the gaseous and volatile products from the decompositions are summarized in Table II. In benzene and more polar solvents, the major liquid product was identified as 2-methoxypropene which strongly suggests heterolytic cleavage of the O–O bond¹¹ of I. In benzene and chlorobenzene, small amounts of *t*-butyl alcohol and toluene (~12%) were observed. The yields of these products agree with the estimated fraction radical reaction from the scavenging experiments (~15%) and the decrease in yield of carbon dioxide (13%) when excess galvinoxyl is present.

In cyclohexene the rate is appreciably slower than that in benzene and there is a corresponding change in products. Succinimide is found in 53% yield along with cyclohexyl 2,5-dioxo-1-pyrrolidineperformate (II) (identified by comparison of n.m.r. and infrared spectra with those of an authentic sample) in 45% yield and *t*-butyl alcohol and bicyclohexenyl are major products. It thus appears that the decomposition of I occurs mainly by heterolysis in benzene and mainly by homolysis in cyclohexene.

The stability¹³ of I and the apparent reluctance of the corresponding carboxyl radical to decarboxylate seem to indicate that the succinimidyl radical is not highly resonance stabilized.¹⁴ More extensive con-

(4) P. D. Bartlett and R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).

(5) E. T. O'Brien, F. Marshall, and R. B. Mesrobian, *ibid.*, **81**, 1506 (1959).

(6) Satisfactory analyses and spectra have been obtained.

(7) D. Verdin, *Trans. Faraday Soc.*, **56**, 823 (1960); T. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964); R. C. Lamb and J. G. Pacifici, *J. Am. Chem. Soc.*, **86**, 914 (1964).

(8) P. D. Bartlett and T. Funahsi, *ibid.*, **84**, 2596 (1962).

(9) The decomposition of I followed by the infrared method appears to be autocatalytic in some solvents and subject to induced decomposition in others. Both effects are apparently eliminated by the presence of 2 *M* styrene.

(10) We are indebted to Mr. C. E. Klopfenstein and Mr. C. Wilkins for making their Fortran program for least-squares treatment of kinetic data available to us.

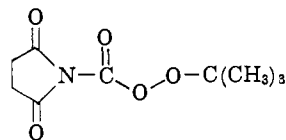
(11) R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948).

(12) P. D. Bartlett and T. B. Gortler, *J. Am. Chem. Soc.*, **85**, 1858 (1963).

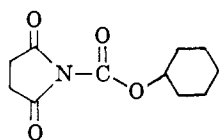
(13) Our preliminary studies on the decomposition of *t*-butyl *N*-ethylpercarbamate indicate it decomposes five times faster than I at 100°. Data in ref. 5 indicate *t*-butyl *N*-phenylpercarbamate decomposes 100 times faster than I at 100° ignoring solvent effects.

(14) H. J. Dauben and L. L. McCoy, *J. Am. Chem. Soc.*, **81**, 4863 (1959).

clusions cannot be made until more is known about percarbamate decompositions. No evidence of acyl isocyanate¹⁵ or any similar fragmentation was found in any of our studies.



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Acknowledgment.—This work was supported by a grant (Type G) from the Petroleum Research Fund administered by the American Chemical Society.

(15) J. C. Martin and P. D. Bartlett, *J. Am. Chem. Soc.*, **79**, 2533 (1957); H. W. Johnson and D. E. Bublitz, *ibid.*, **80**, 3150 (1958).

(16) National Science Foundation Undergraduate Research Participant, 1963-1964.

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Concerning the Mechanism of the Reaction of Phenyl(trihalomethyl)mercurials with Olefins

Sir:

We have reported a facile synthesis of *gem*-dihalo-cyclopropanes by the reaction of phenyl(trihalomethyl)mercurials with olefins.^{1,2} Several comments concerning the possible mechanism of this reaction have appeared.³

Studies of the stereochemistry of the haloform-butoxide-olefin reaction⁷ and of the relative reactivities of olefins toward this reagent system⁸ led to the conclusion that the reaction of a free, electrophilic dihalocarbene with the olefin was involved. Qualitative studies of relative reactivities of olefins toward sodium trichloroacetate in 1,2-dimethoxyethane suggested that there also a reaction between a free carbene and an olefin was taking place.⁹ It therefore was of interest to investigate the stereochemistry of the C₆H₅HgCX₃-olefin reaction and to determine relative reactivities of various olefins toward C₆H₅HgCX₃.

We have compared olefin reactivities toward C₆H₅HgCCl₂Br¹⁰ in benzene at 80° with the reactivities of the same olefins toward sodium trichloroacetate in 1,2-dimethoxyethane at 80°, thus avoiding complications due to temperature effects.¹¹ In the standard ex-

periment 15 ml. of benzene was added to 10.0 mmoles of mercurial under argon, then 50.0 mmoles each of cyclohexene and olefin A. The flask was immersed in a preheated oil bath and the mixture was stirred for 3 hr. and filtered. The filtrate was distilled *in vacuo* into a receiver at -78°. Gas chromatographic analysis of an aliquot of the distillate containing *n*-butyrophenone as internal standard followed.¹² The relative rates (cyclohexene = 1) were calculated by Doering's method.^{8b} The reactions with sodium trichloroacetate were carried out in a similar fashion.

The results of these experiments are given in Table I. The following are worthy of special comment. (1) Especially noteworthy is the near identity of the relative reactivities of all olefins toward C₆H₅HgCCl₂Br and CCl₃CO₂Na. (2) The relative reactivity of olefins toward C₆H₅HgCCl₂Br does not appear to be solvent dependent (note the experiments with (C₂H₅)₂C=CHCH₃ and *trans*-*n*-C₃H₇CH=CHC₂H₅). (3) The relative reactivities parallel reasonably well those measured for similar (but not identical) olefins toward the CHCl₃-*t*-BuOK system,^{8b} but with a greater spread of reactivities being observed in the latter case. Other subtle differences are apparent. These may reflect the effect of lower temperature in the latter system, as well as minor differences in steric factors in the olefins. (4) The relative reactivities do not parallel those observed for iodomethylzinc iodide reactions with comparable olefins,¹³ where the relative reactivities indicated electrophilic attack on the olefin but with a pronounced steric factor also operative. (5) The relative reactivities do not parallel those observed for oxymercuration of olefins.¹⁴ (6) The stereochemistry of the olefin is retained. *cis*- and *trans*-3-heptene gave 1,1-dichloro-2-ethyl-3-*n*-propylcyclopropanes which were identical with the cyclopropanes prepared from the respective olefins by the Doering-Hoffmann method.¹⁵ Similar results were obtained in the reactions of C₆H₅HgCBr₃ with *cis*- and *trans*-2-butene.

The results of our studies lead us to the following conclusions. A "methylene transfer" system of the type discussed by Simmons, *et al.*,¹⁶ does not appear to be involved in the mercurial-olefin reaction: the steric factor associated with iodomethylzinc iodide is absent. Secondly, if in both systems studied by us structures such as I were involved in transition states such as II, then for a number of reasons one would not expect to find such close correspondence in the relative

(1) D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

(2) D. Seyferth, R. J. Minasz, A. J. H. Treiber, J. M. Burlitch, and S. R. Dowd, *ibid.*, **28**, 1163 (1963).

(3) For example, one paper⁴ quotes a referee who asserts that "the mercury reagents most probably do not generate anything approaching free dihalocarbene, but are analogous to the Simmons-Smith reagent." On the other hand, a carbene mechanism is favored by Hine⁵ and by Landgrebe.⁶

(4) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 56 (1964), footnote 16b.

(5) J. Hine, "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964, p. 54.

(6) J. A. Landgrebe and R. D. Mathis, *J. Am. Chem. Soc.*, **86**, 524 (1964).

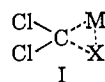
(7) (a) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956); (b) W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956).

(8) (a) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (b) W. von E. Doering and W. A. Henderson, *ibid.*, **80**, 5274 (1958).

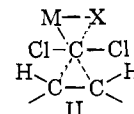
(9) W. M. Wagner, H. Kloosterziel, and S. Van Der Ven, *Rec. trav. chim.*, **80**, 740 (1961).

(10) D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, **84**, 1757 (1962).

(11) The relative reactivities of olefins toward the CHCl₃-*t*-BuOK system were measured at -20 to -10°. ^{8b}



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reactivities of the olefins studied toward C₆H₅HgCCl₂Br (M = C₆H₅Hg) and CCl₃CO₂Na (M = Na). Nor would one expect such good correspondence in relative reactivities for these olefins if CCl₃CO₂Na

(12) The dichlorocyclopropanes were identified by comparison of their g.l.c. retention times and infrared spectra with those of authentic samples. They will be described in a later paper.

(13) E. P. Blanchard and H. E. Simmons, *J. Am. Chem. Soc.*, **86**, 1337 (1964).

(14) C.-E. Döring and H. G. Hausthal, *J. prakt. Chem.*, [4] **22**, 59 (1963).

(15) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954).

(16) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).