

Anal. for $C_8H_{10}OS$: C, 55.3; H, 7.7; S, 24.6. Found: C, 55.6; H, 8.2; S, 24.25.

The allylthioacetone (324 g., 2.5 moles) was converted to allylsulfonylacetone by oxidation with peracetic acid as described above. The product was fractionated to give 330 g. (82% yield) of allylsulfonylacetone, b.p. 115° (1.2 mm.), n_D^{20} 1.4820.

Anal. Calcd. for $C_8H_{10}O_3S$: C, 44.5; H, 6.2; S, 19.7. Found: C, 44.3; H, 6.5; S, 20.07.

5-Phenyl-2-pentene.—To a flask equipped for a batch pyrolysis was added 193 g. (0.96 mole) of 3-benzylsulfonyl-1-butene. The pressure in the system was reduced to 50 mm. and the temperature of the sulfone in the reaction flask was raised to 210° . Heating was continued for 5 hours, during which time 85 g. of distillate was collected in the receiver and 5 g. of trap material after the sulfur dioxide had been evaporated. The two distillates were combined, washed with a 5% sodium hydroxide solution, and fractionally distilled. There was obtained 43 g. (32% yield) of material, b.p. $63-65^\circ$ (5 mm.), n_D^{20} 1.5028-1.5032. The product, 5-phenyl-2-pentene, was identified by elemental analyses (Found: C, 90.2; H, 9.8. Calcd.: C, 90.4; H, 9.6), mass spectrometric and infrared analyses.

***o*-Allyltoluene.**—This experiment was conducted using the equipment for the continuous process. A total of 360 g. (1.83 moles) of allyl *o*-tolyl sulfone was passed through the tube (maintained at $380-388^\circ$) at a rate of about 110 ml./hour. Approximately 288 g. of material was collected in the receiver and 45 g. in the cold trap. The receiver material was distilled and a fraction weighing 89 g. and having a boiling range of 40° (50 mm.) to 105° (10 mm) was collected. This fraction plus 24 g. of trap material from this distillation were combined, washed with 0.5 *N* sodium hydroxide and water, and then fractionally distilled. A 5-g. (2% yield) fraction, boiling range $64-66^\circ$ (10 mm.) and n_D^{20} 1.5138, was identified as *o*-allyltoluene. Infrared spectra showed $CH_2=$ absorption at 3.25μ , $-C=C-$ at

6.1μ , aromatic unsaturation at 6.23 , 6.3 , 6.67μ , and *ortho* disubstitution at 5.15 , 5.25 , 5.57 , 13.47μ . *Anal.* Calcd. for $C_{10}H_{12}$: C, 90.9; H, 9.1. Found: C, 89.9; H, 9.6.

***p*-Allylchlorobenzene.**—*p*-Allylchlorophenyl sulfone (795 g., 3.68 moles) was pyrolyzed in three equal batches at $265-285^\circ$ at 200 mm. for about 2 hours at which time no more distillate could be obtained. The distillates were combined (318 g.) and washed with 1 liter of 10% sodium hydroxide solution to yield 225 g. of material. The organic material was fractionally distilled to yield products boiling from 54° at 2 mm. to 126° at 1 mm. A 5-g. fraction, boiling at $56-57^\circ$ at 2 mm., n_D^{20} 1.5263, was analyzed.

Anal. Calcd. for C_9H_9Cl : C, 70.8; H, 5.9; Cl, 23.3. Found: C, 70.3; H, 5.89; Cl, 21.6. Infrared absorption peaks 3.24 , 3.3 , 5.28 and 5.65μ (assigned to *p*-disubstitution) 5.48 , 6.1 , 6.25 , 6.33 , 6.68 , 11.95 , 12.5μ . Mass spectrometric analyses were consistent with an allylchlorobenzene.

1,9-Decadiene.—This reaction was conducted in a batch type reaction in equipment similar to that described in Example 1. A total of 552 g. (2.07 moles) of 1,4-di-(allylsulfonyl)-butane was heated in the range of 195° (250 mm.) to 260° (150 mm.) for most of the reaction and finally at 180° (2 mm.). The trap material weighing 227 g. and the receiver material weighing 99 g. were combined and washed with dilute sodium hydroxide solution to yield 120 g. of oily layer which was fractionally distilled. There was obtained 41 g. (15% yield) of distillate, boiling range $50-54^\circ$ (10 mm.), n_D^{20} 1.4436-1.4450. Infrared spectra and mass spectrometric analysis indicated the material was predominantly the terminally unsaturated diolefin, 1,9-decadiene, with a small amount of an internally unsaturated compound.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Diacyl Peroxide-Olefin Reactions. Evidence for a Direct Reaction¹

BY FREDERICK D. GREENE, WALDEMAR ADAM² AND JAMES E. CANTRILL

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m,m'-Dibromobenzoyl peroxide and *p,p'*-dimethoxy-*trans*-stilbene react in benzene solution at 45° to afford two 1:1 adducts, shown to be *meso*-dihydroanisoin bis-*m*-bromobenzoate (28%) and the *dl*-diester (57%), in a process that is first order in each reactant. In the presence of the free radical, galvinoxyl, the rate of the peroxide-olefin reaction is reduced by 25%. Evidence of the efficiency of galvinoxyl as a radical scavenger and of its unreactivity toward the dimethoxystilbenes and toward the peroxides employed is presented. It is concluded that the major course of the reaction proceeds by direct reaction between peroxide and olefin, on which is superimposed a radical chain reaction of short chain length. From the increase in consumption of galvinoxyl in the presence of both peroxide and olefin, it has been determined that scavengable radicals are formed in 10% efficiency by the direct reaction of peroxide with olefin. The effect of substituents and solvents on rate indicates a weak response to ionic factors.

Reaction between peroxygen compounds and carbon-carbon unsaturation has long been known in the epoxidation of olefins with peracids.³ Examination of direct reaction between diacyl peroxides and olefins generally is precluded by the facility with which such reactants lead to free radical polymerization, although acyl peroxides and vinyl ethers^{4,5} have been reported to yield diesters in addition to polymers. Evidence for a

direct reaction between acyl peroxides and unsaturation is found in the reaction of the cyclic diacyl peroxide, phthaloyl peroxide, with olefins⁶ and in the recent demonstration by Martin and Drew⁷ of a lack of equivalence in the oxygen-18 distribution between aryl and alkyl oxygen in the cyclohexyl acetate formed from acetyl peroxide-carbonyl-oxygen-18 and cyclohexene. The object of the present study has been the examination of mechanisms in olefin-acyclic diacyl peroxide reactions.

Results

From the effect of substituents on peracid and on olefin in the epoxidation reaction⁸ it was ex-

(6) F. D. Greene and W. W. Rees, *ibid.*, **80**, 3432 (1958).

(7) J. C. Martin and E. H. Drew, Abstracts of the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, p. 8-O.

(8) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

(1) This work was supported by the research program of the Atomic Energy Commission under Contract No. AT(30-1)-905. Reproduction is permitted for any purpose of the United States Government.

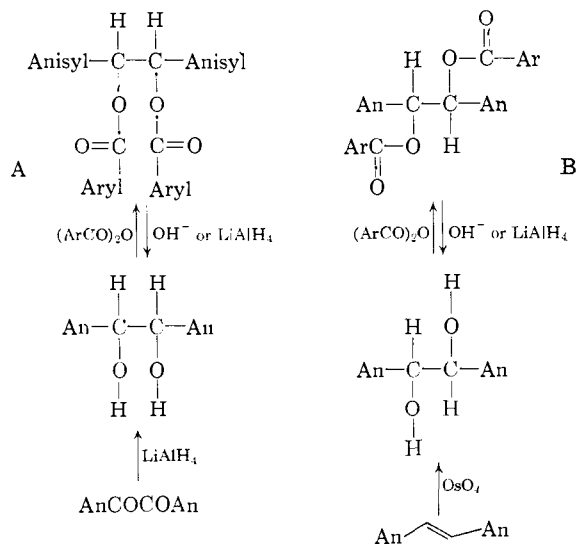
(2) General Electric Fellow 1960-1961.

(3) See D. Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947), and references cited therein.

(4) M. F. Shostakovskii, N. A. Gershtein and V. A. Neterman, *Izvest. Akad. Nauk, S. S. S. R., Otdel. Khim. Nauk*, 1839 (1959).

(5) S. M. McElvain and C. H. Stammer, *J. Am. Chem. Soc.*, **75**, 2154 (1953).

pected that a direct reaction would be most favorable between olefin substituted with electron-donating groups and peroxide substituted with electron-withdrawing groups. The principal system chosen for investigation was *m,m'*-dibromobenzoyl peroxide and *p,p'*-dimethoxy-*trans*-stilbene in benzene at 45°. Under these conditions a moderate reaction occurs affording two one-to-one adducts (A and B) of peroxide and olefin (total yield, 84%) and a small amount of *m*-bromobenzoic acid (7%). The adducts are virtually identical in infrared spectra and show strong absorption at 1720 cm.⁻¹. Compounds A and B are assigned the structures of the *meso*- and the *dl*-di-*m*-bromobenzoates of the corresponding *p,p'*-dimethoxy-stilbenediols (dihydroanisoin bis-*m*-bromobenzoates) on the basis of the evidence summarized in Chart I. Although both diol isomers are reported in the

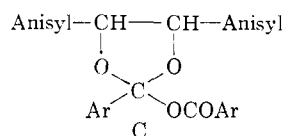


literature, assignment of *meso*- and *dl*-configuration had not been made previously and, indeed, some confusion existed in the literature concerning the physical properties of the lower melting isomer.⁹ The assignment in this study of the *dl*-structure to the lower melting diol is based on the stereospecific synthesis shown. The assignment of the *meso* structure to the higher melting isomer is based on the analogous formation of *meso*-stilbenediol in high yield from the reduction of benzil with lithium aluminum hydride.¹⁰ In agreement with a large number of similar *meso-dl* pairs,¹¹ the *meso* isomer is the higher melting member of the diol and diester pairs. A remaining structural question for A and B not answered by the data of Chart I is a distinction between diester and ortho ester formulations such as C. The choice of diester structures for both A and B rather than structures of type C is based on ultraviolet absorption data. The principal difference between diester and ortho ester is associated with *m*-bromobenzoate absorp-

(9) (a) A. Rossel, *Ann.*, **151**, 41 (1869); (b) M. Tiffeneau and A. Orekhoff, *Bull. soc. chim., France*, [4] **33**, 1832 (1923); (c) J. B. Conant and H. B. Cutter, *J. Am. Chem. Soc.*, **48**, 1016 (1926).

(10) Unpublished results; see also D. J. Cram and F. A. Abd Elhafez, *J. Am. Chem. Soc.*, **74**, 5828 (1952).

(11) R. Stern, Abstracts of the 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957, 5-0.



tion, occurring at 292 m μ with an extinction coefficient of 875 for methyl *m*-bromobenzoate. At this wave length calculated extinction coefficient for diester is 1750 and for ortho ester is 875; observed extinction coefficient is 1700 for both A and B.

The ratio of *meso*- to *dl*-diester was determined by removal of *meso*-diester by fractional crystallization and conversion of residue to a mixture of *meso*- and *dl*-diols which could be analyzed by infrared spectra. The over-all amount of diesters is 28% *meso* and 57% *dl*. Both the *meso*- and *dl*-diesters were shown to be configurationally stable to the reaction conditions. Heating a solution of *meso*- or *dl*-diester in benzene for a prolonged period resulted in considerable destruction of diester and concomitant formation of *m*-bromobenzoic acid. It is believed that the small amount of acid formed in the olefin-peroxide reaction arises by attack by carboxylate radical on diester.

Reaction of *m,m'*-dibromobenzoyl peroxide with *p,p'*-dimethoxy-*cis*-stilbene proceeds more slowly than with the *trans* isomer but affords an almost identical product mixture: 29% *meso*-diester, 57% *dl*-diester and 6% *m*-bromobenzoic acid.

Reaction of *p,p'*-dinitrobenzoyl peroxide with *p,p'*-dimethoxystilbene afforded products similar to that above: principal formation of one-to-one adducts identical in infrared spectra with authentic *meso*- and *dl*-di-*p*-nitrobenzoates of the dimethoxy-stilbenediols prepared by the methods outlined in Chart I.

Kinetics.—The kinetics of the peroxide-olefin reaction have been investigated principally under two sets of conditions: (1) pseudo-first-order conditions with peroxide concentration approximately 0.01 *M* and olefin concentration of 3×10^{-5} *M*, following rate of disappearance of olefin spectroscopically at 329 m μ in the ultraviolet; (2) second-order conditions, following rate of disappearance of olefin spectroscopically and rate of disappearance of peroxide by the usual iodometric method. Demonstration of identity in rate of disappearance of olefin and peroxide is shown in Fig. 1. Evidence for first-order behavior in rate of disappearance of each reactant—peroxide and olefin—is summarized in Table I, covering a ten-

TABLE I

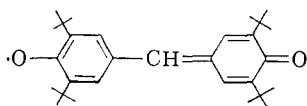
REACTION OF *m,m'*-DIBROMOBENZOYL PEROXIDE (P) WITH *p,p'*-DIMETHOXY-*trans*-STILBENE (S) IN BENZENE AT 44.8°

Reactants, $M \times 10^2$		$k_2 \times 10^3$, $M^{-1} \text{sec.}^{-1}$
P	S	
1.00	1.00	$1.04 \pm 0.03^a, b$
1.00	1.00	$1.08 \pm .04^a$
1.00	0.004	$1.08 \pm .014^a$
2.50	.004	$1.09 \pm .035^a$
5.03	.004	$0.94 \pm .03^a$
0.54	.004	$1.18 \pm .08^a$

^a Spectroscopic for olefin. ^b Titrimetric for peroxide, 1.05 ± 0.03 .

fold variation in peroxide concentration and a 250-fold variation in olefin concentration. All product and kinetic data were obtained from runs carried out under degassed conditions since the olefin is readily consumed in the presence of oxygen.¹²

Consideration of Mechanism.—The product data and the observation of first-order dependence in each reactant are consistent with a large number of mechanisms which may be divided into two principal groups: radical chain reactions and direct reactions. To make this division, the hindered phenoxy radical galvinoxyl,^{13,14} discovered by Coppinger,¹⁵ was employed as a radical scavenger.



Neither the olefin nor the peroxide is attacked by galvinoxyl. The measured consumption of galvinoxyl in twenty-five hours in a solution of the peroxide (0.01 *M*) and galvinoxyl (0.00095 *M*) in benzene at 45° was 3.56×10^{-4} *M*. The decomposition of peroxide in this same time period was calculated to be 1.77%, corresponding to a maximum number of 3.54×10^{-4} *M* radicals. These data indicate that the efficiency of galvinoxyl in capture of radicals derived from peroxide is high and that cage recombination of radicals derived from this peroxide under the reaction conditions must be very low, in agreement with expectations from other studies.¹⁶ Consequently it was possible to utilize galvinoxyl to answer two questions of mechanism in the olefin-peroxide reaction: (1) to what extent are radicals involved in the reaction of peroxide and olefin (determined by examining the effect of the peroxide-olefin pair on the degree of consumption of galvinoxyl, followed spectroscopically at 434 or 775 μ)? (2) If radicals are involved, to what extent do they enter into chain reactions (determined by examining the effect of galvinoxyl on the rate of disappearance of peroxide)? The relationship of these types of effect to mechanism is summarized in Table II.

TABLE II

RELATION OF EFFECT OF SCAVENGER TO MECHANISM		
Mechanism	Predicted effect of galvinoxyl on rate of olefin-peroxide reacn.	Predicted effect of olefin-peroxide reacn. on consumption of galvinoxyl
Radical, chain	Large decrease	Small increase
Radical, non-chain	No effect	Large increase
Non-radical	No effect	No effect

Reaction of olefin and peroxide in the presence of galvinoxyl results in a 25% reduction of rate of disappearance of peroxide (Fig. 1) and a consider-

(12) For evidence on the copolymerization of oxygen with styrene and indene, see A. A. Miller and F. Mayo, *J. Am. Chem. Soc.*, **78**, 1017 (1956); G. A. Russell, *ibid.*, **78**, 1035 (1956).

(13) P. D. Bartlett and C. Ruchardt, *ibid.*, **82**, 1756 (1960).

(14) Contrary to previous reports [ref. 15 and M. S. Kharasch and B. S. Yoshi, *J. Org. Chem.*, **22**, 1435 (1957)], galvinoxyl is not stable to oxygen. The galvinoxyl-oxygen reaction will be treated in a forthcoming publication.

(15) G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 501 (1957).

(16) G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950); D. F. DeTar and R. C. Lamb, *ibid.*, **81**, 122 (1959); C. G. Swain, L. J. Schaad and A. J. Kresge, *ibid.*, **80**, 5313 (1958).

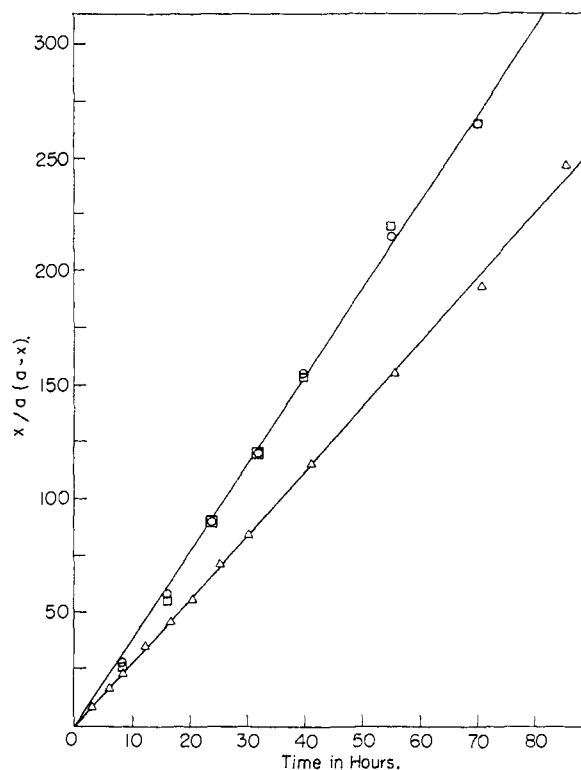


Fig. 1.—Reaction of *m,m'*-dibromobenzoyl peroxide (0.01 *M*) with *p,p'*-dimethoxy-*trans*-stilbene (0.01 *M*) in benzene (degassed) at 44.8°: O, rate of disappearance of peroxide (titrimetric); □, of olefin (spectroscopic); Δ, of peroxide in presence of galvinoxyl (titrimetric).

able increase in consumption of galvinoxyl over that observed with the peroxide-galvinoxyl pair alone. Over the range of an eightfold variation in initial galvinoxyl concentration, the amount of galvinoxyl consumed is constant, suggestive that galvinoxyl is capturing all statistically-distributed radicals. Secondly, the rate constant for disappearance of peroxide in the presence of the varying initial concentrations of galvinoxyl is reduced to a constant value. These data are summarized in Table III.

TABLE III

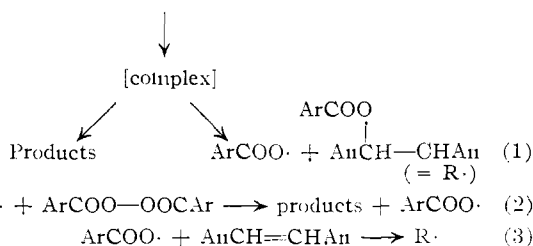
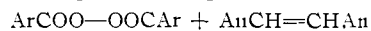
REACTION OF *m,m'*-DIBROMOBENZOYL PEROXIDE (P) WITH *p,p'*-DIMETHOXY-*trans*-STILBENE (S) IN THE PRESENCE OF GALVINOXYL (G) IN BENZENE AT 44.8°

Reactants, $M \times 10^2$	Galvinoxyl consumption in 8 hr., %	Radicals scavenged in 8 hr., $M \times 10^4$	$k_2 \times 10^3$ $M^{-1} \text{sec.}^{-1}$ (titrimetric)		
P	S	G			
1	0	0.095	11.5	1.09	^a
1	1	0			1.05
1	1	0.0475	97.5	4.64	0.78
1	1	.095	49	4.65	.77
1	1	.095	49	4.64	.79
1	1	.190	24.5	4.65	.79
1	1	.380	12.4	4.75	.79

^a $k_1 = 1.98 \times 10^{-7}$ sec.^{-1} .

The interpretation placed on these data is that in the absence of galvinoxyl, peroxide disappears by direct reaction with olefin (eq. 1) and by chain reaction (eq. 2 and 3). In the presence of galvinoxyl the chain carriers are efficiently scavenged

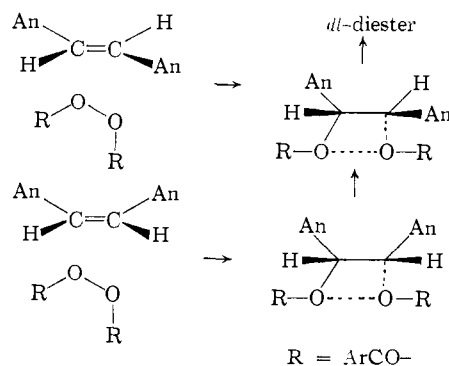
and the rate of disappearance of peroxide is reduced to the rate of the direct reaction between peroxide and olefin (plus the rate of unimolecular decomposition of the peroxide; in a solution of the peroxide and olefin, initially 0.01 *M* in each component and in the absence of galvinoxyl, the ratio of the initial rate of disappearance of peroxide by reaction with olefin to the rate of disappearance of peroxide by unimolecular decomposition is forty to one). The increase in consumption of galvinoxyl in the presence of both peroxide and olefin over that in the presence of just the peroxide indicates that, in addition to radical formation by unimolecular decomposition of peroxide, *scavengeable radicals are being formed in low efficiency by the direct reaction of peroxide and olefin.* In the absence of galvinoxyl, the radicals effect further destruction of olefin and peroxide by a chain process. The ratio of consumption of peroxide by direct reaction to consumption by chain reaction, determined from the rate constants in the presence and absence of scavenger (*e.g.*, lines 2 and 3 of Table III), is three to one. Under the conditions of Table III, peroxide is consumed to the extent of 18% in eight hours from which it may be derived that for every two *scavengeable radicals* formed in the absence of galvinoxyl, approximately three molecules each of peroxide and olefin are removed. (The rate of disappearance of both the olefin and the peroxide are higher, and equal, in the absence of galvinoxyl.)



Although the lack of information on the possible intermediacy of ortho esters renders interpretation of the *meso-dl*-diester product ratios from the *cis*- and *trans*-olefins rather speculative, it may be pointed out that induced decomposition of the peroxide (eq. 2) might be expected to afford *meso*-diester in preference to *dl*.¹⁷ Formation of the (more stable) *meso*-diester in only 29% yield from either olefin is consistent with formation of this product principally by the induced decomposition route. The preferential formation of *dl*-diester from *cis*-dimethoxystilbene seems unexpected but may be due to rotation of the anisyl groups away from each other prior to formation of the final carbon-oxygen bond.

The fraction of effective collisions between olefin and peroxide that lead to *scavengeable radicals* may be determined from the data of Table III. The difference between the number of radicals scavenged by galvinoxyl in a given period of time (an eight-hour period was chosen) in the presence and absence of olefin but with identical initial concentrations of peroxide and galvinoxyl (first and fourth lines of Table III) represents the

(17) F. D. Greene, W. A. Remers and J. W. Wilson, *J. Am. Chem. Soc.*, **79**, 1416 (1957).



number of *scavengeable radicals* produced by the reaction of peroxide with olefin, and is seen to be $3.56 \times 10^{-4} M$ (4.65 - 1.09). The *maximum* number of radicals that might be produced by reaction of peroxide with olefin in this same time period, calculated on the basis of formation of two radicals from each destructive encounter of peroxide with olefin, is $35.3 \times 10^{-4} M$. Thus, approximately 10% of the effective collisions of peroxide with olefin leads to *scavengeable radicals*. The degree of radical pair formation at the stage preceding radical escape may be higher than this value of 10%, but the data of these experiments are uninformative on the vexing question of product formation *via* cyclic processes *vs.* cage recombination. More amenable to experiment is the question of the nature of the transition state of the peroxide-olefin reaction. Replacement of one of the methoxyl groups of the dimethoxystilbene by hydrogen results in a 33-fold decrease in rate of reaction with *p,p'*-dinitrobenzoyl peroxide. Replacement of both *m*-bromo groups by *p*-nitro groups in the peroxide results in a ninefold increase in rate of reaction with the *p,p'*-dimethoxystilbene. This increase has been shown to be associated with an increase in the *direct* reaction between olefin and peroxide rather than with an increase in the radical chain part of the reaction by a detailed examination of the galvinoxyl-olefin-peroxide system exactly parallel to that described above for *m,m'*-dibromobenzoyl peroxide. The effect of substituents on the peroxide-olefin reaction is comparable to that observed in a number of unimolecular and bimolecular peroxygen reactions, but is substantially smaller than the effects observed with reactions involving ionization at a benzoyl position [rearrangement of decalyl perbenzoates in methanol at 24.6° , $\rho = +1.34^{18}$; decomposition of *t*-butyl arylperacetates¹⁸ in toluene at 56° , ρ (*vs.* σ^+) = -1.20; reaction of stilbenes with perbenzoic acids in benzene at 30° , ρ (substituted peracids) = +1.30⁸, ρ (*vs.* σ^+ , substituted stilbenes) = -0.84^{8,19}; reaction of stilbenes with benzoyl peroxides (this work), ρ (substituted peroxide) = +1.2, ρ (*vs.* σ^+ , substituted stilbenes) = -1.0]. The peroxide-olefin reaction shows some dependence on medium but, again, the effect is small (reaction of *m,m'*-dibromobenzoyl peroxide with *p,p'*-dimethoxystilbene at 45° , relative rates: benzene, 1; chloroform, 3.3; acetonitrile, 8.5; rearrangement of decalyl perbenzoate,²⁰

(18) P. D. Bartlett and J. L. Kice, *ibid.*, **75**, 5591 (1953).

(19) D. R. Campbell, J. O. Edwards, J. MacLachlan and K. Polgar, *ibid.*, **80**, 5308 (1958).

relative rates: benzene, 1; chloroform, 7; acetonitrile, 20; rearrangement of camphene hydrochloride,²¹ relative rates: benzene, 1; acetonitrile, 120). Thus, for the peroxide-olefin reaction both substituent effects and solvent effects are suggestive of some, but minor, ionic character to the transition state. The kinetic data are summarized in Table IV.

TABLE IV
REACTION OF SUBSTITUTED BENZOYL PEROXIDES WITH SUBSTITUTED STILBENES AT 44.8°

Peroxide	Reactants, $M \times 10^3$ Olefin	Solvent	$k_2 \times 10^2$, $M^{-1} \text{sec.}^{-1}$
Di-Br ^a (10)	<i>cis</i> -DiMeO ^b (10)	C ₆ H ₆	0.04 ^c
Di-Br ^a (1.0)	<i>trans</i> -DiMeO ^d (1.0)	C ₆ H ₆	1.05 ^c
Di-NO ₂ ^f (1.0)	<i>trans</i> -DiMeO ^d (1.0)	C ₆ H ₆	9.58 ^c
Di-NO ₂ ^f (1.0)	<i>trans</i> -DiMeO ^d (1.0)	C ₆ H ₆	7.55 ^{c,g}
Di-NO ₂ ^f (4.0)	<i>trans</i> -MonoMeO ^h (5.0)	C ₆ H ₆	0.29 ^c
Di-Br ^a (0.85)	<i>trans</i> -DiMeO ^d (0.0032)	CHCl ₃	3.5 ^c
Di-Br ^a (1.0)	<i>trans</i> -DiMeO ^d (0.0030)	CH ₃ CN	8.90

^a *m,m'*-Dibromobenzoyl. ^b *p,p'*-Dimethoxy-*cis*-stilbene. ^c Spectroscopic. ^d *p,p'*-Dimethoxy-*trans*-stilbene. ^e Titrimetric. ^f *p,p'*-Dinitrobenzoyl. ^g In the presence of 9.6×10^{-4} galvinoxyl. ^h *p*-Methoxy-*trans*-stilbene.

With regard to the driving force for the reaction of *m,m'*-dibromobenzoyl peroxide with *p,p'*-dimethoxy-*trans*-stilbene, the question may be raised of the extent to which π -complexing of the aryl units of peroxide with aryl units of olefin facilitates the reaction.²² Although some help may be obtained in this way, the principal driving force must be associated with direct reaction of the peroxy group with the double bond since purely aliphatic olefins also have been found to undergo direct reaction with diacyl peroxides.²³

It is of interest to note the relation of the results of this study to those of reactions of diacyl peroxides with other electron-rich sources. The closest analogy is found in the reaction of diacyl peroxides with tertiary amines²⁴⁻²⁶ in which peroxide and substrate also undergo a direct reaction leading, in low efficiency, to free radicals as indicated by analysis of rates of initiation of polymerization.²⁵ The reactions of diacyl peroxides with secondary amines²⁷ to afford *O*-acyl hydroxylamines and with phosphines²⁸ to afford anhydrides and phosphine oxides find closer analogy to the reaction of diacyl peroxides with aliphatic olefins which will be described in a forthcoming publication.²³

Experimental

Substituted benzoyl peroxides used in this research were prepared by the method of Swain, Stockmayer and Clarke.²⁹

- (20) R. Criegee and R. Kaspar, *Ann.*, **560**, 127 (1948).
 (21) H. Meerwein and K. van Emster, *Ber.*, **55**, 2507 (1922).
 (22) A detailed examination of the ultraviolet and visible regions of the spectrum failed to reveal spectral evidence for a complex.
 (23) F. D. Greene and W. Adam, in preparation.
 (24) R. Huisgen, W. Heydkamp and F. Bayerlein, *Ber.*, **93**, 363 (1960).
 (25) C. Walling and N. Indictor, *J. Am. Chem. Soc.*, **80**, 5815 (1958).
 (26) L. Horner and C. Betzel, *Ann.*, **579**, 175 (1953).
 (27) R. Huisgen and F. Bayerlein, *ibid.*, **630**, 138 (1960); D. B. Denney and D. Z. Denney, *J. Am. Chem. Soc.*, **82**, 1389 (1960).
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The purity was determined iodometrically; material of at least 99% purity was used.

p,p'-Dimethoxy-*trans*-stilbene is best prepared from anisalazine.³⁰ After repeated crystallization from benzene, material of m.p. 210–211° (lit.³⁰ m.p. 213–214°) was obtained, λ_{max} in chloroform 329 m μ (ϵ 25,400).

Anisil was prepared from anisole and oxalyl chloride by the method of Staudinger.³¹ Material of m.p. 131–132° (lit.³¹ m.p. 132–133°) was isolated.

meso-Dihydroanisoin.—To a slurry of 0.5 g. (0.0158 mole) of lithium aluminum hydride in 15 ml. of freshly distilled tetrahydrofuran, cooled to –40°, was added over 15 minutes a solution of 6.5 g. (0.024 mole) of anisil in 75 ml. of tetrahydrofuran. After stirring at –40° for an hour, the excess lithium aluminum hydride was decomposed by adding ethyl acetate. The reaction mixture was worked up by pouring it into 20 volumes of water and collecting the precipitate on a fluted filter. The precipitate was triturated with methylene chloride to remove the organic material from the aluminum hydroxide. The combined methylene chloride triturates were dried over anhydrous magnesium sulfate, filtered, and the methylene chloride was evaporated at reduced pressure. The residue was recrystallized from a methylene chloride-pentane mixture yielding 2.7 g. (41% yield), m.p. 168–170° (lit.³² m.p. 170–171°).

meso-Dihydroanisoin bis-*m*-bromobenzoate was prepared by the Brewster procedure.³³ To a solution of 0.402 g. (0.002 mole) of *m*-bromobenzoic acid (m.p. 155–157°) in 5 ml. of pyridine was added with cooling 0.763 g. (0.004 mole) of *p*-toluenesulfonyl chloride (m.p. 66–68°), followed by 0.274 g. (0.001 mole) of *meso*-dihydroanisoin. The flask was stoppered and stored at 10° overnight. The solution was poured onto 10 ml. of ice-water and filtered. The residue was dissolved in methylene chloride and dried over anhydrous magnesium sulfate. After filtration, pentane was added to the methylene chloride solution to precipitate the product: 0.5 g. (78% yield), m.p. 152–154°. Repeated recrystallization from a methylene chloride-pentane mixture afforded material of constant m.p. 155–156°.

Anal. Calcd. for C₃₀H₂₄Br₂O₈: C, 56.37; H, 3.78; Br, 24.96. Found: C, 56.10; H, 3.76; Br, 24.72.

Anisaldehyde cyanohydrin was prepared according to the method of Levine, *et al.*³⁴ Material of m.p. 65–68° (lit.³⁵ m.p. 66–67°) was obtained in a 98% yield.

p-Methoxyphenylacetic acid was synthesized by the general procedure of Levine.³⁴ Material of m.p. 84–85° (lit.³⁶ m.p. 85–86°) was isolated in a 34% yield.

cis- α -(*p*-Methoxyphenyl)-*p*-methoxycinnamic Acid.—To a solution of 25 g. (0.15 mole) of *p*-methoxyphenylacetic acid in 20 ml. of acetic anhydride and 20 ml. of triethylamine was added 30 g. (0.22 mole) of *p*-methoxybenzaldehyde. The reaction mixture was heated at reflux for 100 minutes. After cooling to room temperature, 40 ml. of concd. hydrochloric acid was added and a stiff paste resulted. This paste was dissolved in 1.5 l. of chloroform. The chloroform solution was washed well with water and then evaporated to dryness. The residue was triturated with 1.2 l. of a 2% aqueous sodium hydroxide solution. Almost all of the solids dissolved. With continuous stirring by means of a magnetic stirrer, the alkaline solution was neutralized with acetic acid to pH 6. (Great care must be taken in this neutralization.) If one neutralizes the solution by adding the acetic acid all at once, a thick paste results which is unfilterable. It is recommended that the acetic acid be added dropwise until pH 7 is reached. The precipitate is collected on a Büchner funnel, and the filtrate is further acidified until the pH of the solution is 6. Both solids are identical and have a m.p. 216–218°. The combined solids were dissolved in chloroform and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed at reduced pressure until crystallization started. A white compound, 25 g. (59% yield), m.p. 216–218°, was isolated. This solid was recrystallized from a water-methanol mixture; m.p. 217–218°.

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Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.81; H, 5.67. Found: C, 71.45; H, 5.78.

p,p'-Dimethoxy-*cis*-stilbene.—To a solution of 20 g. (0.0705 mole) of *cis*- α -(methoxyphenyl)-*p*-methoxycinnamic acid in 30 ml. of dry quinoline was added 1.5 g. of copper chromite catalyst. The contents of the flask were heated to 220–233° for 15 min. After allowing the reaction mixture to cool to room temperature, 500 ml. of ether was added. The ethereal solution was extracted with 10% aqueous hydrochloric acid until the aqueous extract showed little coloration. The ether solution was washed several times with a saturated aqueous sodium chloride solution. After drying over anhydrous magnesium sulfate, the ether solution was boiled twice with decolorizing carbon, affording a pale yellow solution. The ether was removed at reduced pressure. To the residual oil several volumes of *n*-hexane were added yielding a white solid, 0.8 g. (4.7% yield), m.p. 209–211°, shown to be *p,p'*-dimethoxy-*trans*-stilbene by means of infrared spectra and mixture melting point with the authentic compound. Attempts to crystallize the residue proved difficult. The compound was finally purified by elution chromatography on an alumina column. A slightly yellowish oil, 7.4 g. (43.8% yield), was obtained which crystallized on standing, m.p. 34–36° (lit.³⁷ m.p. 37°). This substance was then recrystallized from pentane at 0°, affording material of m.p. 35.5–36.0°, λ_{max} in chloroform 296 μ (ϵ 14,800).

d,l-Dihydroanisoin.—To a solution of 4.72 g. (0.0197 mole) of *p,p'*-dimethoxy-*trans*-stilbene in 550 ml. of pyridine was added 5.0 g. (0.0197 mole) of osmium tetroxide with stirring. The oxblood-red solution was stirred for an hour. The pyridine was removed at reduced pressure to a final volume of 110 ml. To this solution, 9.0 g. of sodium bisulfite in 150 ml. of water containing 50 ml. of pyridine was added. After 20 minutes of vigorous stirring, the reaction mixture was extracted with 500 ml. of chloroform. The chloroform solution was washed well with water and dried over anhydrous magnesium sulfate. After filtration, the chloroform was evaporated at reduced pressure. The residue was recrystallized from an ether-pentane mixture, affording a white compound, 3.5 g. (65.3% yield), m.p. 122–123° (lit. 110°,³⁸ 125–126°,³⁹ 98–101°^{9c}). In the second and third crop a total of 0.65 g. (12.1% yield) of product was obtained, m.p. 119–121°.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 70.05; H, 6.62. Found: C, 69.85; H, 6.60.

d,l-Dihydroanisoin bis-*m*-bromobenzoate was prepared by the method described above for the *meso*-diester using a 48-hr. reaction period. The crude product was crystallized from ethanol; m.p. 101.5–103.5°, yield 60%.

Anal. Calcd. for $C_{20}H_{22}Br_2O_6$: C, 56.37; H, 3.78; Br, 24.96. Found: C, 56.26; H, 3.79; Br, 24.60.

d,l-Dihydroanisoin mono-*p*-nitrobenzoate was obtained by application of the method described above for the diesters but allowing only a 3-hr. reaction time before dilution with water. The yellow residue was repeatedly recrystallized from a methylene chloride-pentane mixture, affording 0.15 g. (35.5% yield) of a yellow solid, m.p. 155.5–156.0°. The infrared spectrum showed ester absorption at 3580 cm^{-1} . The ultraviolet spectrum in ethanol showed a maximum at 265 μ (ϵ 16,300). The compound gave an analysis corresponding to *d,l*-dihydroanisoin mono-*p*-nitrobenzoate.

Anal. Calcd. for $C_{23}H_{21}NO_7$: C, 65.34; H, 5.00; N, 3.31. Found: C, 65.27; H, 4.81; N, 3.09.

d,l-Dihydroanisoin bis-*p*-nitrobenzoate was obtained by use of a 12-hr. reaction period for the esterification procedure described above. Recrystallization from a chloroform-petroleum ether mixture afforded a yellow, crystalline substance, 0.529 g. (92.5% yield), m.p. 93–101°. Repeated recrystallizations did not raise the melting point of this substance. However, when the molten material in the melting point tube was allowed to resolidify and the melting point retaken, the substance melted sharply at 163–164°. Also, recrystallization from an ethanol-petroleum ether mixture yielded material of m.p. 163–164°. The ultraviolet spectrum in ethanol shows a maximum at 262 μ , ϵ 31,500.

Anal. Calcd. for $C_{30}H_{24}N_2O_{10}$: C, 62.93; H, 4.22; N, 4.89. Found: C, 62.68; H, 4.22; N, 4.75.

meso-Dihydroanisoin bis-*p*-nitrobenzoate was prepared by the above method with a 3-hr. reaction period. After pouring the reaction mixture onto 30 g. of ice, the precipitate was collected on a Büchner funnel, washed well with water and pressed dry on a porous plate. The product was dissolved in methylene chloride and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated at reduced pressure. The yellow solids were recrystallized from a methylene chloride-pentane mixture. Repeated recrystallization afforded 0.3623 g. (63.3% yield), m.p. 189–190°, of a pale yellow solid. The ultraviolet spectrum of this compound showed a maximum in ethanol at 263 μ , ϵ 31,300.

Anal. Calcd. for $C_{30}H_{24}N_2O_{10}$: C, 62.93; H, 4.22; N, 4.89. Found: C, 62.71; H, 4.43; N, 4.88.

Reaction of *m,m'*-Dibromobenzoyl Peroxide and *p,p'*-Dimethoxy-*trans*-stilbene.—To a dry, constricted test-tube was added 1.3333 g. (0.00333 mole) of *m,m'*-dibromobenzoyl peroxide and 0.8000 g. (0.00333 mole) of *p,p'*-dimethoxy-*trans*-stilbene. The solids were dissolved in 35 ml. of freshly distilled benzene. The tube was degassed on the vacuum line by freezing the contents with a Dry Ice-trichloroethane freezing mixture and evacuating the tube to 0.05 mm. pressure. The tube was shut off from the vacuum line and allowed to warm up to room temperature and then refrozen. This process was repeated three times and the tube was sealed under vacuum. The tube was placed into the constant temperature bath at 80° and vigorously shaken to dissolve the solids. After 24 hr. of reaction time, the tube was removed from the bath and allowed to cool to room temperature. Iodometric titration of an aliquot (0.1 ml.) of this solution indicated that all of the peroxide had reacted.

The benzene was evaporated at reduced pressure. An infrared spectrum of this residual semi-solid was identical to the spectra of *d,l*- and *meso*-dihydroanisoin bis-*m*-bromobenzoates (the *d,l*- and *meso*-diesters are virtually identical in the infrared spectrum in chloroform from 4000–400 cm^{-1}).³⁸ The residue was dissolved in 50 ml. of methylene chloride and extracted with 5% aqueous sodium bicarbonate until all extractable materials were removed, *i.e.*, until the extract showed no precipitation on acidification. The combined extracts were acidified and extracted with chloroform. The chloroform solution was dried over magnesium sulfate. After filtration, the solvent was evaporated at reduced pressure. A white compound, 0.093 g. (7 mole % based on original moles of peroxide), m.p. 156–157°, was isolated. This solid was proved to be *m*-bromobenzoic acid by mixture melting point and infrared spectrum.

The neutral methylene chloride solution was dried over magnesium sulfate. After filtration, the solvent was evaporated at reduced pressure. The residual oil was dissolved in 5 ml. of ether. On standing, within a few minutes a white precipitate formed. The substance, 0.532 g. (24.9% based on initial moles), m.p. 140–152°, was collected and recrystallized from ethanol, yielding 0.482 g. of a white compound, m.p. 154–156°. This compound was shown to be *meso*-dihydroanisoin bis-*m*-bromobenzoate by mixture melting point and infrared spectrum. To the ethereal mother liquor was added petroleum ether and the solution was scratched with a glass rod until crystallization started. A second white compound, 0.42 g. (13.2% yield), m.p. 88–96°, was obtained. The infrared spectrum of this material was identical with that of the authentic *d,l*-dihydroanisoin bis-*m*-bromobenzoate. Repeated recrystallization from ethanol afforded a material which melted at 96–104°. A mixture melting point of this substance with the authentic *d,l*-diester showed no depression.

In a second experiment, the ethereal mother liquor was diluted to 10 ml. with ether. To this solution was added 0.38 g. (0.01 mole) of lithium aluminum hydride. The flask was protected with a drying tube. The reaction mixture was stirred for 3 hr. at room temperature. Wet ether was added slowly to decompose the lithium aluminum hydride and the aluminum alcoholate complex. The resulting slurry was well triturated alternately with 15-ml. portions of ether and 15-ml. portions of methylene chloride for ten triturations. The combined triturates were dried over anhydrous magnesium sulfate. After filtration, the solvent was removed at reduced pressure affording an oil, 1.09 g. An infrared spectrum in chloroform showed no carbonyl absorption but strong hydroxyl absorption. This oil was triturated with

(38) We wish to thank Mr. Isaacson for the determination of the infrared spectra in the region 700–400 cm^{-1} .

(37) W. Schlenk and E. Bergmann, *Ann.*, **463**, 123 (1928).

5-ml. portions of *n*-pentane until all pentane-soluble material was removed. To the residual semi-solid was added 5 ml. of ether. A white solid, 62.1 mg., m.p. 115–145°, was isolated. An infrared spectrum was identical to the addition spectrum of approximately 48% *meso*- and 52% *d,l*-dihydroanisoin. This solid was recrystallized from an ether-pentane mixture, and a white substance, 0.030 g. (3.3 mole % based on initial moles), m.p. 167–171°, was isolated. Infrared spectrum and mixture melting point proved it to be the *meso*-dihydroanisoin.

TABLE V

REACTION OF *m,m'*-DIBROMOBENZOYL PEROXIDE^a WITH *p,p'*-DIMETHOXY-*trans*-STILBENE^b IN THE PRESENCE OF GALVINOXYL^c IN BENZENE AT 44.8°

Time, sec. × 10 ⁻²	Ml. S ₂ O ₈ ²⁻	Ml. S ₂ O ₈ ²⁻ for G ^d	O.D. ₄ (λ 775 mμ)	k ₂ × 10 ³ , M ⁻¹ sec. ⁻¹
0.0	10.55	0.45	0.545	...
10.8	9.70	.36	.433	0.753
21.6	8.92	.27	.335	.827
28.8	8.55	.23	.278	.745
43.2	7.68	.15	.188	.789
57.6	7.15	.08745
72.0	6.62	.04745
90.0	5.95	.02780
108.0	5.50	.01778
144.0	4.75	.00783
198.0	4.00	.00773
252.0	3.50	.00750
306.0	2.95	.00789

$$k_2 = 0.773 \pm 0.0199 \times 10^{-3} M^{-1} \text{ sec.}^{-1}; \% \text{ av. dev.} = 2.56\%$$

^a 0.01 M initial concn. ^b 0.01 M initial concn., ^c 0.0009 M initial concn. ^d Galvinoxyl titer.

The mother liquors from the *meso*-dihydroanisoin were combined. By means of repeated fractional crystallization with *n*-pentane a total of 0.4154 g. (45.5 mole % based on initial moles), m.p. 105–115°, was isolated. Recrystallization from ether afforded material of m.p. 118–121°, which was identified by infrared spectrum and mixture melting point as *d,l*-dihydroanisoin. The mother liquors from the fractional crystallization were evaporated and triturated with *n*-pentane. Another 0.105 g. (11.5 mole % based on initial moles), m.p. 95–105°, was obtained. The infrared spectrum of this substance was identical with that of *d,l*-dihydroanisoin.

Reaction of *p,p'*-Dimethoxy-*cis*-stilbene with *m,m'*-Dibromobenzoyl Peroxide in Benzene.—To a dry, constricted test-tube was added 2 g. (0.005 mole) of *m,m'*-dibromobenzoyl peroxide and 1.2 g. (0.005 mole) of *p,p'*-dimethoxy-*cis*-stilbene. By means of a syringe 5 ml. of dry benzene was introduced into the test-tube. The tube was degassed as described previously and sealed under vacuum. The tube was placed into the constant temperature bath at 80° and vigorously shaken to dissolve the solids. After 24 hr. of reaction time, the tube was removed from the bath and worked up similarly to the reaction of *p,p'*-dimethoxy-*trans*-stilbene with *m,m'*-dibromobenzoyl peroxide. Iodometric analysis of an aliquot of the benzene solution indicated that all peroxide had reacted. An infrared spectrum of the crude reaction mixture in chloroform was identical with that of *d,l*- and *meso*-dihydroanisoin bis-*m*-bromobenzoate. The benzene solution was extracted with 5% aqueous sodium bicarbonate, yielding 0.109 g. (5.5 mole % based on initial moles of peroxide), m.p. 156–158°, of *m*-bromobenzoic acid was isolated.

The neutral benzene solution was dried over anhydrous magnesium sulfate and the solvent removed by evaporation at reduced pressure. The residual semi-solid was dissolved in 15 ml. of ether, and on standing 0.7873 g. (24.6 mole % based on initial moles), m.p. 145–152°, of a white solid was collected. This solid was identified as the *meso*-dihydroanisoin bis-*m*-bromobenzoate by infrared spectrum and mixed melting point.

The ethereal mother liquor was treated with 0.42 g. (0.011 mole) of lithium aluminum hydride and worked up as described above, yielding 0.050 g. (3.7 mole % based on orig-

inal moles) of *meso*-dihydroanisoin and 0.77 g. (56% yield) of *d,l*-dihydroanisoin.

Reaction of *p,p'*-Dinitrobenzoyl Peroxide with *p,p'*-Dimethoxy-*trans*-stilbene.—To a dry, constricted test-tube was added 0.8305 g. (0.0025 mole) of *p,p'*-dinitrobenzoyl peroxide and 0.6 g. (0.0025 mole) of *p,p'*-dimethoxy-*trans*-stilbene. To the solids was added 50 ml. of dry benzene. The tube was degassed and sealed under vacuum. It was placed in the constant temperature bath at 44.8° and allowed to react for 28 hr. A precipitate was formed during the reaction. The tube was allowed to cool to room temperature and the benzene solution was filtered. The yellow solid, 0.112 g., m.p. 230–235°, was *p*-nitrobenzoic acid. On evaporation at reduced pressure to 10-ml. volume, another 0.0223 g., m.p. 220–235°, of *p*-nitrobenzoic acid was isolated. On further evaporation to 3-ml. volume, 0.174 g. of a yellow solid, m.p. 83–107°, was collected. This substance was recrystallized from chloroform, and 0.081 g., m.p. 90–101°, was reisolated. Upon repeated recrystallization from ethanol, 0.0245 g., m.p. 149–162°, of a pale yellow compound was obtained. This compound was identified as *d,l*-dihydroanisoin bis-*m*-bromobenzoate by infrared spectrum and mixture melting point. The infrared spectrum (KBr) of the crude reaction product was identical with the spectra of *d,l*- and *meso*-dihydroanisoin bis-*p*-nitrobenzoates (the infrared spectra of these two isomers in chloroform are virtually identical from 4000–400 cm.⁻¹).³⁸

Stability of *meso*- and *d,l*-Dihydroanisoin Bis-*m*-bromobenzoates to *m*-Bromobenzoic Acid under the Reaction Conditions.—To a dry, constricted test-tube was added 0.160 g. (0.000025 mole) of *meso*-dihydroanisoin bis-*m*-bromobenzoate and 0.016 g. of *m*-bromobenzoic acid. After 5 ml. of dry benzene was added, the tube was degassed and sealed under vacuum. It was placed in a constant temperature bath at 80° for 70 hr. The benzene solution was extracted with 5% aqueous sodium bicarbonate and 15 mg. of *m*-bromobenzoic acid was reisolated. The benzene solution was dried over magnesium sulfate and the solvent removed under reduced pressure. The residue, 0.160 g., m.p. 146–148°, was shown by means of infrared and ultraviolet spectrum to be identical with the original *meso*-diester. Recrystallization from ethanol afforded material of m.p. 155–156° (pure *meso*-diester, m.p. 155–156°).

Subjecting a 0.160-g. sample of *dl*-diester to the above conditions led to 0.016 g. of *m*-bromobenzoic acid, m.p. 156–158°, and 0.158 g. of *dl*-diester, m.p. 98–102°.

Reaction of *meso*- and *d,l*-Dihydroanisoin Bis-*m*-bromobenzoates with *m,m'*-Dibromobenzoyl Peroxide.—To a dry, constricted test-tube was added 0.040 g. (0.0001 mole) of *m,m'*-dibromobenzoyl peroxide and 0.064 g. (0.0001 mole) of *meso*-dihydroanisoin bis-*m*-bromobenzoate. By means of a syringe, 5 ml. of dry benzene was added. The test-tube was degassed, sealed under vacuum, and placed in the constant temperature bath at 80° for 3 days. The reaction mixture was worked up by extracting the benzene solution with 5% aqueous sodium bicarbonate. On acidification of the basic extract and extraction with methylene chloride, 0.016 g. (40% yield based on moles of peroxide), m.p. 155–157°, of *m*-bromobenzoic acid was isolated. An ultraviolet spectrum of the crude reaction product showed that the spectrum was considerably changed in the region from 240–290 mμ from the spectrum of the original *meso*-diester.

Subjecting 0.040 g. (0.0001 mole) of *m,m'*-dibromobenzoyl peroxide and 0.064 g. (0.0001 mole) of *d,l*-dihydroanisoin bis-*m*-bromobenzoate in 5 ml. of benzene to the above conditions afforded 0.0152 g. (38% yield based on the initial moles of peroxide), m.p. 155–157°, of *m*-bromobenzoic acid. The ultraviolet spectrum of the crude reaction product in chloroform differed greatly in the region 240–290 mμ from the original *d,l*-diester.

Stability of *meso*- and *d,l*-Dihydroanisoin to Aqueous Methanolic Potassium Hydroxide.—To 10 ml. of a solution of 20% aqueous methanol, containing 1.0 g. of potassium hydroxide, was added 0.100 g. (0.000356 mole) of *meso*-dihydroanisoin. While allowing nitrogen to pass through the solution, the reaction mixture was refluxed for 4 hr. The solution remained colorless during this time. Then 10 ml. of water was added, and, on cooling, 0.0875 g. (87.5% yield), m.p. 170–172°, of *meso*-dihydroanisoin was reisolated. An analogous experiment was carried out with the *d,l*-dihydroanisoin. However, with *d,l*-dihydroanisoin the reaction mixture had to be extracted with methylene chloride. From

0.100 g. (0.000356 mole) of *d,l*-dihydroanisoin, 0.070 g. (70% yield), m.p. 118–120°, was reisolated.

Saponification of *meso*- and *dl*-Dihydroanisoin Bis-*m*-bromobenzoates.—To 10 ml. of 20% aqueous methanol containing 1.0 g. of potassium hydroxide was added 0.420 g. (0.000657 mole) of *meso*-dihydroanisoin bis-*m*-bromobenzoate. While allowing nitrogen to pass through the solution, the reaction mixture was brought to reflux for 5 hr. The reaction mixture was diluted with 30 ml. of water and cooled to room temperature. The precipitate, 0.1723 g. (96% yield), m.p. 164–169°, was collected. This substance was identified as the *meso*-dihydroanisoin by infrared spectrum and mixture melting point. The aqueous basic solution was acidified and extracted with methylene chloride. After drying over magnesium sulfate and removal of the solvent at reduced pressure, 0.197 g. (75% yield), m.p. 140–150°, of *m*-bromobenzoic acid was obtained.

Hydrolysis of the *dl*-di-ester required a reaction time of 12 hr. By extraction of the reaction mixture with methylene chloride and drying of the extract, 0.115 g. (84% yield), m.p. 112–118°, of *d,l*-dihydroanisoin was isolated, identified by mixture melting point and infrared spectrum. The aqueous solution was acidified and extracted with chloroform. After drying over magnesium sulfate and evaporation of the solvent, 0.150 g. (74% yield), m.p. 145–155°, of *m*-bromobenzoic acid was obtained.

Galvinoxyl was prepared by a modification of the procedure of Coppinger.¹⁵ A solution of 42.4 g. (0.1 mole) of 3,5,3',5'-tetra-*t*-butyl-4,4'-dihydroxydiphenylmethane in 500 ml. of benzene was deaerated by passing a stream of nitrogen through the solution for 2 hr. With stirring under nitrogen, 108 g. (0.45 mole) was isolated. On repeated recrystallization from benzene or *n*-pentane under nitrogen atmosphere, 1.0 g. of material was obtained of dec. pt. 158° (dependent on rate of heating); λ_{\max} in benzene, 434 m μ (ϵ 145,000), 530 m μ (broad shoulder ϵ 1020), 775 m μ (ϵ 580). Galvinoxyl obeys Beer's law at the wave lengths examined. An iodometric titration of galvinoxyl (see below) showed that it was $97 \pm 1.0\%$ pure. The infrared spectrum was missing the bands at 3670 and 1519 cm.⁻¹; however, a faint shoulder at 1620 cm.⁻¹ was detected. Since these bands are due to hydrogalvinoxyl, it seems probable that no more than 5% hydrogalvinoxyl is present as an impurity in the galvinoxyl.

Iodometric Titration of Galvinoxyl.—Into a clean, dry 125-ml. stoppered erlenmeyer flask was weighed a sample of galvinoxyl. The galvinoxyl was dissolved in 2 ml. of chloroform or 3 ml. of benzene. To this solution 13 ml. of acetic

acid (anal. reagent) was added and the solution was degassed by adding crushed Dry Ice. After the solution reached room temperature, approximately 1 g. of solid sodium iodide (anal. reagent) was added. The entire sample was diluted with 45 ml. of deaerated water and placed in the dark for 5 min. The solution was titrated with standard sodium thiosulfate solution until near the end-point. Starch indicator (2 ml.) was added and the sample titrated until the blue starch-iodine color just disappeared. A 35.1-mg. sample of galvinoxyl required 7.95 ml. of 0.01 *N* thiosulfate, indicating a purity of 95.5%.

Stability of the Dimethoxystilbenes to Galvinoxyl.—A degassed benzene solution of galvinoxyl at 45° underwent 2.5% decrease in the 775 m μ band in 90 hr. A degassed benzene solution of galvinoxyl (0.00095 *M*) and *p,p'*-dimethoxy-*trans*-stilbene (0.01 *M*) at 45° underwent 3.5% decrease in the 775 m μ (galvinoxyl) band and 1% increase in the 329 m μ (olefin) band in 90 hr. A degassed benzene solution of the galvinoxyl (0.002 *M*) and the *cis*-olefin (0.002 *M*) underwent no change at 434 m μ (galvinoxyl) and no increase at 329 m μ (*i.e.*, no isomerization of *cis*- to *trans*-olefin) in 24 hr.

Kinetic Method. Titrimetric and Spectrophotometric Determination of Rates of Reaction of Peroxides and Olefins.—All kinetic runs were degassed on the vacuum line to at least 0.1 mm. pressure by the method described in the product studies. The tubes were placed in a constant temperature bath, removed at intervals, and quenched in a water-ice mixture. An aliquot was removed and added to a solution of sodium iodide in acetic acid, degassed with Dry Ice. The titration procedure was that described above for galvinoxyl. For spectrophotometric determinations, an aliquot of the kinetic solution was removed by a lambda-pipet, diluted with the solvent to the desired concentration, and the optical density measured on a Beckman DU spectrophotometer at the desired wave length. Average deviation in rate constants by both titrimetric and spectrophotometric procedures was about 2–3%. A sample run, including galvinoxyl, is shown in Table V. The results are summarized in Tables I, III and IV.³⁹

Acknowledgment.—We wish to thank the Ethyl Corporation for a generous sample of 3,5,3',5'-tetra-*t*-butyl-4,4'-dihydroxydiphenylmethane.

(39) All of the original kinetic data are reported in the doctoral thesis of W. Adam, M.I.T., February, 1961.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY, DURHAM, N. C.]

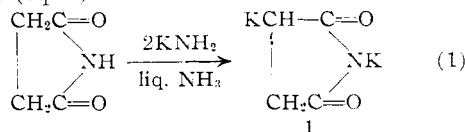
Condensations at the α -Carbon of Succinimide Through its Dipotassio Salt Prepared by Means of Potassium Amide

BY DAVID R. BRYANT¹ AND CHARLES R. HAUSER

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Three types of condensations were effected at the α -carbon of succinimide through its dipotassio salt, which was prepared by means of two molecular equivalents of potassium amide in liquid ammonia. They involved benzoylation with benzoyl chloride, aroylations with aromatic esters, and aldol condensations with benzophenone and anisaldehyde. These preferential reactions at the carbanion of the dipotassio salt rather than at its imide anion resulted in new products or furnished new routes for synthesis of known compounds.

This paper describes three types of condensations at the α -carbon of succinimide through its dipotassio salt I, which was prepared by means of two molecular equivalents of potassium amide in liquid ammonia (eq. 1).



These condensations are similar to those observed recently² with the dipotassio salts of certain

(1) National Science Foundation Predoctoral Fellow, 1958–1961.

(2) C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6380 (1958), and T. M. Harris and C. R. Hauser, *ibid.*, **81**, 1160 (1959).

β -diketones such as acetylacetone, to which succinimide is related as a cyclic nitrogen analog.

Benzoylation of dipotassio salt I was effected with benzoyl chloride to form the C-benzoyl derivative II in 16–29% yield (eq. 2).

