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A Series of Tertiary Butyl Peresters Showing Concerted Decomposition

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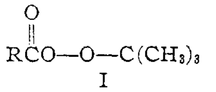
RECEIVED OCTOBER 2, 1957

A series of *t*-butyl peresters is described which undergo thermal decomposition at rates parallel to the stability of the free radical R in the formula $RCOOOC(CH_3)_3$. Evidence is presented that the thermal decomposition of these esters involves the simultaneous rupture of an O–O and C–C bond with the formation of carbon dioxide in the primary step. Quantitative studies are reported of the products of decomposition and of the rates and kinetics at different temperatures. The series shows decreases in entropy of activation accompanying decreases in energy of activation and a mechanistic interpretation of this parallelism is given. *t*-Butyl peracetate and perbenzoate are believed to undergo primary cleavage only at the O–O bond while *t*-butyl trifluoroperacetate appears to undergo ionic rearrangement instead. The first-order rate constants of these peresters at 60° cover a range of 10^5, the activation enthalpies a range of 15 kcal. and the activation entropies a range of 22.9 e.u.

It is known that the primary act in the decomposition of benzoyl peroxide is the simple rupture of the oxygen–oxygen bond, since essentially 100% of the starting material has been recovered as benzoic acid in the presence of iodine and moist carbon tetrachloride[1] without the interceptor influencing the rate or kinetic form of the decomposition. On the other hand, the greatly accelerated decomposition of the peroxide related to phenylacetic acid[2] points to the existence of a concerted decomposition mechanism which allows the resonance energy of the benzyl radical to contribute to the energy level of the transition state. The preparation of other acyl peroxides having this property in higher degree is limited by the exceedingly low temperatures at which it is necessary to work. Simons and Feldman[3] in this Laboratory have shown by the study of *t*-butyl phenylperacetate, trimethylperacetate, trichloroperacetate and diphenylperacetate that here too the possibility of concerted generation of a somewhat stabilized radical permits the extrusion of carbon dioxide in the primary step of the decomposition and that here a wider range of structure can be observed than among the acyl peroxides. We have prepared for comparative kinetic and product study seven further peresters of the type I where R = trifluoromethyl, methyl, β-styryl, cinnamyl, 2-phenyl-2-propyl, 1,1-diphenylethyl and α-phenylallyl. Named in ascending order of decomposition velocity, these peresters cover a range of 10^5 in their first-order rate constants for decomposition referred to the common temperature of 60°. They are all prepared by the low-temperature reaction of *t*-butyl hydroperoxide with the corresponding acid chloride in the presence of excess of anhydrous pyridine. The products are mostly liquids which were purified by extraction, low-temperature vacuum distillation or chromatography and whose identity was established by elementary analysis and their purity by examination of the infrared absorption spectra, usually rather sensitive to the presence of the most common contaminants. The peresters all liberate iodine from an acidified solution of potassium iodide but this reaction is in general not quantitative, presumably because of the sensitivity of these peresters to acids. The kinetics of their decomposition could be satisfactorily followed by observing the decrease in the sharp and intense carbonyl absorption at 5.65 μ which is sufficiently displaced to encounter little interference from ketonic or carboxylic reaction products. The reaction products in chlorobenzene, the solvent used for the kinetic studies, were separated by condensation of the gases, distillation of the liquids and chromatography of the solids, and identified by comparison with authentic specimens, usually by means of infrared spectra. The results of the product analyses are shown in Tables II–VIII.



$$R\overset{O}{\overset{\|}{C}}O{-}O{-}C(CH_3)_3$$

I

Kinetic Results

Table I summarizes the kinetic information on the new peresters together with four others recently prepared in this Laboratory[3] and three familiar initiators for comparison. The figure in the second column is the half-life in minutes at 60° either measured directly or extrapolated from measurements at two or more temperatures, leading to the activation parameters listed in the third and fourth columns. $\Delta H^{\ddagger}$, the enthalpy of activation, is obtained by multiplying R (1.987 calories per degree) by the slope of the line obtained when ln (k/T) is plotted against $1/T$. $\Delta S^{\ddagger}$, the entropy of activation, is then obtained by substituting this value of $\Delta H^{\ddagger}$ and the values of k and T for any point on the drawn line into the equation

$$k = \frac{k'T}{h} e^{\Delta S^{\ddagger}/R} e^{\Delta H^{\ddagger}/RT}$$

Evidence for Concerted Decomposition

In the first place the dependence upon structure of decomposition rate and activation energy for decomposition throughout this series constitutes the best evidence that here the alkyl radical from the acid part of the perester is being formed during the rate-determining step of the decomposition. Thus we must revive the mechanism of decomposition into three fragments which has been often quoted for benzoyl peroxide and which, as we have seen, does not fit the facts in that particular case.

The compounds listed in Table I include several series which show some regularities in the effects of structure. First there is the sequence: di-*t*-butyl peroxide, *t*-butyl perbenzoate, benzoyl per-

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[1] G. S. Hammond and L. M. Soffer, THIS JOURNAL, **72**, 4711 (1950).

[2] P. D. Bartlett and J. E. Leffler, *ibid.*, **72**, 3030 (1950).

[3] D. M. Simons and A. M. Feldman, unpublished work in this Laboratory.

TABLE I

DECOMPOSITION RATES OF PERESTERS $RCOOOC(CH_2)_3$ COMPARED WITH THREE FAMILIAR INITIATORS

Solvent: chlorobenzene except where noted

R	Half-life at 60°, min.	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, cal. per degree
(Di-*t*-butyl peroxide)	10^7	37.8	13.8[a]
CH_3	5×10^5	38	17
C_6H_5	3×10^4	33.5	7.8[b]
(Benzoyl peroxide)	6000	32.7	13.3[c,e]
$C_6H_5CH_2$	1700	28.7	3.9[f]
Cl_3C	970	30.1	8.9[f]
$(CH_3)_3C$	300	30.6	13[f]
$C_6H_5CH{=}CHCH_2$	100	23.5	−5.9[e]
$(C_6H_5)_2CH$	26	24.3	−1.0[f]
$((C_6H_5)N{=}NC(C_6H_5)_3)$	18	28.3	11.4[d]
$C_6H_5(CH_3)_2C$	12	26.1	5.8
$(C_6H_5)_2CH_3C$	6	24.7	3.3
$C_6H_5(CH_2{=}CH)CH$	4	23.0	−1.1

[a] In *t*-butylbenzene. Calculated from data of J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 1337 (1948). [b] In *p*-chlorotoluene; A. T. Blomquist and A. F. Ferris, *ibid.*, **73**, 3408 (1951). [c] In benzene; K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946). [d] M. G. Alder and J. E. Leffler, *ibid.*, **76**, 1426 (1954). [e] Corrected or induced decomposition. [f] Reference 3.

oxide, covering a range of over a thousandfold in their half-lives and of 5.1 kcal. in their enthalpies of activation. Since this increase in decomposition rate through the series cannot be attributed to concerted decomposition, it must be the result of a somewhat greater stabilization of the benzoate radical as compared to the *t*-butoxy radical.

TABLE II

PRODUCTS OF DECOMPOSITION OF *t*-BUTYL PERACETATE IN CHLOROBENZENE AT 140°

Perester decomposed, 0.522 g., 3.95 mmoles; product recovered, 0.530 g., 102%; carbon dioxide, 77%; acetic acid, 23%.

	Mg.	Mmoles	Mole/mole of perester
Carbon dioxide	135	3.06	0.77
Acetone	169	2.91	.73
Methane	30	1.87	.47
Carbon monoxide	1	0.04	.01
Isobutylene	3	.05	.01
Ethane[a]	3	.12	.03
Acetic acid	55	.91	.23
Tar	134		
t-Butyl alcohol	None		

[a] Incomplete identification.

In the series R = CH_3, $C_6H_5CH_2$, $(C_6H_5)_2CH$ we note a similar acceleration covering a range of more than 10^4 and associated with a total drop in activation enthalpy of 13.7 kcal. Similarly in the series R = *t*-butyl, cumyl, α,α-diphenylethyl there is a smaller but progressive acceleration covering a 50-fold range of rate constant and a 5.9 kcal. span in $\Delta H^{\ddagger}$. These regularities can scarcely mean other than a concerted decomposition in which the resonance energy of the benzyl, benzhydryl, cumyl and α,α-diphenylethyl radicals contributes substantially to lowering the energy level of the transition state.

TABLE III

PRODUCTS OF DECOMPOSITION OF *t*-BUTYL TRIFLUOROPERACETATE

Perester decomposed in carbon tetrachloride, 0.89 g., 4.8 mmoles, at 100°

	Mmole	Mole/mole of perester
Carbon dioxide	0.18	0.037
Chlorotrifluoromethane	.31	.065
Trifluoromethane	.02	.004
Isobutylene	.08	.016
Trifluoroacetic acid	2.2	.460

Perester decomposed without solvent, 1.211 g., 6.51 mmoles at 35°; product recovered 1.165 g., 96%

	Mg.		
Carbon monoxide	5	0.18	0.027
Methane	3	.18	.027
Carbon dioxide	9	.20	.031
Acetone	181	3.1	.480
Trifluoroacetic acid	514	4.5	.690
t-Butyl trifluoroacetate	157	0.9	.140
Methyl trifluoroacetate	114	.9	.140
t-Butyl acetate	9	.08	.012
Methyl acetate	7	.08	.012
Tar	165		

TABLE IV

PRODUCTS OF DECOMPOSITION OF *t*-BUTYL PERCINNAMATE IN CHLOROBENZENE AT 120°

Perester decomposed, 0.689 g., 3.13 mmoles; product recovered, 0.653 g., 95%; carbon dioxide, 70%; acid, 16%.

	Mg.	Mmoles	Mole/mole of perester
Carbon dioxide	97	2.20	0.70
Acetone	134	2.31	.74
Methane	2	0.14	.04
Cinnamic acid	72	0.49	.20
Oil, unidentified	50		
Tar	300		
t-Butyl alcohol	None		

TABLE V

PRODUCTS OF DECOMPOSITION OF *t*-BUTYL PHENYLDIMETHYLPERACETATE IN CHLOROBENZENE AT 60°

Perester decomposed, 0.408 g., 1.72 moles; product recovered, 0.390 g., 95%; carbon dioxide, 99%; acid residue, 102%; *t*-butyl residue, 92%.

	Mg.	Mmoles	Mole/mole of perester
Carbon dioxide	75	1.70	0.99
Acetone	25	0.44	0.25
t-Butyl alcohol	64	.87	.50
Cumene	12	.10	.06
α-Methylstyrene	23	.19	.11
Tetramethylbibenzyl	139	.59	.34
t-Butyl α,α-dimethylbenzyl ether	52	.27	.17

Still slightly more rapid in its decomposition is the perester *t*-butyl 1-phenyl-2-propene-1-percarboxylate which, on concerted decomposition, can yield the phenylallyl radical. This radical can also result from the isomeric perester *t*-butyl 3-phenyl-2-propene-1-percarboxylate in which a primary, instead of a secondary, allylic bond is broken in the rate-determining step. In the latter case the value of the rate constant increased with increasing perester concentration and the half-life, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ listed in the table are those obtained when the first-order component of the rate was

TABLE VI

PRODUCTS OF DECOMPOSITION OF *t*-BUTYL α,α-DIPHENYLPERPROPIONATE IN CHLOROBENZENE AT 50°

Perester decomposed, 0.611 g., 2.05 mmoles; product recovered, 0.563 g., 92%; carbon dioxide, 97%; acid residue, 94%; *t*-butyl residue, 77%.

	Mg.	Mmoles	Mole/mole of perester
Carbon dioxide	87	1.98	0.97
Acetone	26	0.45	.22
t-Butyl alcohol	72	.97	.47
1,1-Diphenylethane	118	.64	.31
1,1-Diphenylethylene	118	.64	.31
2,2,3,3-Tetraphenylbutane	109	.32	.16
t-Butyl α-methylbenzhydryl ether	40	.16	.08

TABLE VII

PRODUCTS OF DECOMPOSITION OF *t*-BUTYL 2-PHENYL-3-PERBUTENOATE IN CHLOROBENZENE AT 60°

Perester decomposed, 1.625 g., 6.945 mmoles; product recovered, 1.575 g., 97%; carbon dioxide, 74%; undecomposed isomeric perester, 16%.

	Mg.	Mmoles	Mole/mole of perester
Carbon dioxide	227	5.17	0.74
Acetone	76	1.31	.19
Methane	2	0.14	.02
t-Butyl alcohol	218	2.94	.42
1,4-Diphenylhexadiene-1,5	155	0.65	.09
t-Butyl cinnamyl ether	104	0.54	.08
Carbonyl compound calculated as *t*-butyl 2-phenyl-2-perbutenoate	263	1.12	0.16
Oil, unidentified	124		
Tar	410		
Acid	None		
Dicinnamyl	None		
Propenylbenzene	None		
Allylbenzene	Less than 5		

TABLE VIII

PRODUCTS OF DECOMPOSITION OF *t*-BUTYL 4-PHENYL-3-PERBUTENOATE IN CHLOROBENZENE AT 80°

Perester decomposed, 1.076 g., 4.60 mmoles; product recovered, 1.036 g., 96%; carbon dioxide, 81%; carbonyl compounds from acid residue, 19%.

	Mg.	Mmoles	Mole/mole of perester
Carbon dioxide	163	3.71	0.81
Acetone	78	1.35	.29
Methane	3	0.18	.04
t-Butyl alcohol	133	1.80	.39
1,4-Diphenylhexadiene-1,5	156	0.57	.12
t-Butyl 4-phenyl-2-perbutenoate[a]	127	.54	.12
2-*t*-Butoxy-4-phenyl-γ-butyrolactone[a]	76	.33	.07
Oil, unidentified	160		
Tar	143		
Acid	None		
Dicinnamyl	None		
Allylbenzene	None		

[a] Incomplete identification.

estimated by the method of Nozaki and Bartlett.[4] The difference between the rate constants for the two isomers resides mostly in the entropy term and may easily be connected with the greater freedom of rotation which exists in the primary, as compared with the secondary, starting molecule and is lost in the transition state.

Fate of the Radicals

Table IX summarizes some of the pertinent facts about the decomposition products of two peresters where the yield of carbon dioxide was 97–99%. According to the mechanism of concerted decomposition which we favor, *t*-butyl α-phenylisoperbutyrate and α,α-diphenylperpropionate should yield, respectively, the cumyl and α,α-diphenylethyl free radicals whose behavior in solution has been observed in experiments in which they were generated from quite different sources.[5–8] In both cases the radical R is accounted for in four different products: coupling product, saturated and unsaturated hydrocarbon from disproportionation and *t*-butyl aralkyl ether. The fact that coupling product predominates with the cumyl radical is consistent with previous observations that coupling of this radical competes successfully with disproportionation. The same is true of the α,α-diphenylethyl radical, but here the coupling at ordinary temperatures is reversible[8] and the longer the coupling product is held in the absence of oxygen the more disproportionation occurs in the free radicals in equilibrium with the coupling product. The excess of olefin over paraffin in the former case probably indicates capture of β-hydrogen from the radical by the *t*-butoxy radical. Finally, the amount of ether observed sets an upper limit upon the operation of the "cage effect"[9] or any intramolecular mechanism for decomposition of the perester. Thus in the case of $R = (C_6H_5)_2CCH_3$, 92–93% of the decompositions lead to fully free α,α-diphenylethyl radicals.

TABLE IX

EFFECT OF STRUCTURE ON FATE OF RADICALS FROM PERESTER $RCOOOC(CH_3)_3$ DECOMPOSED IN CHLOROBENZENE SOLUTION

R	T, °C.	% of total R appearing as RH	Olefin	RR	Ether
$C_6H_5C(CH_3)_2$	60	5.8	11	68.6	15.7
$CH_3(C_6H_5)_2C$	50	31	31	31	7.8

As early observed by Raley, Rust and Vaughan,[10] acetone and *t*-butyl alcohol result from the *t*-butoxy radical in a ratio which is influenced by the temperature and by the presence of efficient hydrogen donors in the solution. In our decompositions at 60° the ratio of *t*-butyl alcohol to acetone was near two. In one experiment at 80° (Table VIII) this ratio was 1.3, while at 120° and above (Tables II and IV) the ratio dropped to zero.

Products from the Unsaturated Peresters

The decomposition products of the two esters yielding the phenylallyl radical are unusually complicated, the source of the complication appear-

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(4) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

(5) M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945).

(6) M. S. Kharasch and W. H. Urry, *ibid.*, **13**, 101 (1948).

(7) K. Ziegler, *Ann.*, **551**, 127 (1942).

(8) K. Ziegler, R. B. Whitney and P. Herte, *ibid.*, **551**, 187 (1942).

(9) M. S. Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

(10) J. H. Raley, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **70**, 1337 (1948).

ing to be the ready isomerization of each of these esters into its isomer having the double bond conjugated with the carboxyl group. These peresters which cannot yield allylic radicals by concerted decomposition are comparable in stability with *t*-butyl peracetate and remain completely undecomposed during the kinetic runs. This competing isomerization is not the cause of the failure of the straight-chained ester to follow first-order kinetics; for the isomerization, which should also be a process of the first order, would be interpreted by our infrared technique as a decomposition, the ester absorption being moved out of the region observed during the kinetic determinations. According to the product analysis, the measured rates should be corrected by at least 12–16% for this isomerization, but this was not done in view of the incomplete identification of the products and uncertainty as to the exact amount of isomerization. From both isomeric peresters yielding the phenylallyl radical the only coupling product found was the unsymmetrical product 1,4-diphenyl-1,5-hexadiene. This might be regarded as an example of the preferential rate of bond formation between centers of differing electronegativities or, alternatively, as a compromise between favorable electron availability at the secondary position and the low steric requirement at the primary. The fact that *t*-butyl cinnamyl ether was found only from the decomposition of the branched perester may suggest a competing and complicating mechanism of internal decomposition, but the amount of this ether was so small and the product mixture so complex that it seems an inadequate basis for drawing any such conclusion.

Two Exceptional Peresters

t-Butyl percinnamate was examined as an analog of the conjugated perester formed by isomerization of the compounds just discussed. *t*-Butyl trifluoroperacetate was made for comparison with the trichloroperacetate which shows accelerated decomposition. Both of these peresters required high temperatures for their decomposition as does *t*-butyl peracetate. Both showed a strong dependence of decomposition rate in chlorobenzene upon initial concentration of perester and are hence not included in the kinetic table. The 70% yield of carbon dioxide and 16% yield of acid from *t*-butyl percinnamate is consistent with a decomposition by an unconcerted free radical mechanism. On the other hand, *t*-butyl trifluoroperacetate showed an entirely different behavior, both its kinetics and its products being completely foreign to those of the other peresters in this series. It showed an extreme degree of solvent dependence, the rate constants in sealed tubes at 100.6° for comparable concentrations in pentane, carbon tetrachloride and chlorobenzene being respectively 0.16, 1.0 and 26.5, all $\times 10^{-4}$ sec.$^{-1}$. The rate and concentration dependence were reduced by decomposition in the presence of pyridine. This perester is its own best solvent for purposes of rapid decomposition; slow in solvents at 90°, the decomposition is rapid in the homogeneous liquid at 35°. Only 3.1% of the possible carbon dioxide is evolved. The largest single product is trifluoroacetic acid, 69%, with 28% of trifluoroacetic esters being present. This general pattern of kinetics and decomposition products is far more consistent with an ionic rearrangement of the Criegee[11] type than with any kind of decomposition into free radicals. Although ionic rearrangements of *t*-butyl peresters have not previously been observed, recent work by Mr. B. T. Storey in this Laboratory has provided evidence that when the related acid is strong enough such rearrangement does indeed take place.

Radical Stabilization and Decomposition Rate

Figure 1 represents with an energy diagram the manner in which stabilization of a radical which begins to be formed in the initial act of decomposition can increase the rate of that decomposition and lower its activation energy. The upper line represents the continuous increase in free energy attendant upon gradual stretching of this oxygen-oxygen bond of a peroxide or perester in which only this bond breaks in the rate-determining step. There is a slight hump in the curve representing the fact that two free radicals can never combine without some small requirement in activation energy and in orientation. The height of the hump then represents the free energy of activation for the decomposition and the vertical distance to the horizontal part of the curve represents the ΔF of dissociation into two radicals. If now one of these radicals, for example a carboxylate radical, is rather unstable relative to carbon dioxide and a new alkyl radical, the stretching of its carbon–carbon bond can be represented on the same graph as a descending line which begins at the level of the dissociation products and descends with increasing degree of bond stretch. The crossing of such a descending curve with the original ascending curve then establishes a new hump which represents the lower activation energy of a concerted decomposition, in case it is possible for the O–O bond and the C–C bond to become stretched simultaneously in a geometry compatible with the incipient formation of a carbon dioxide molecule. The greater the energy gained from decarboxylation, the greater will be the lowering of the energy hump and the more rapid the concerted decomposition.

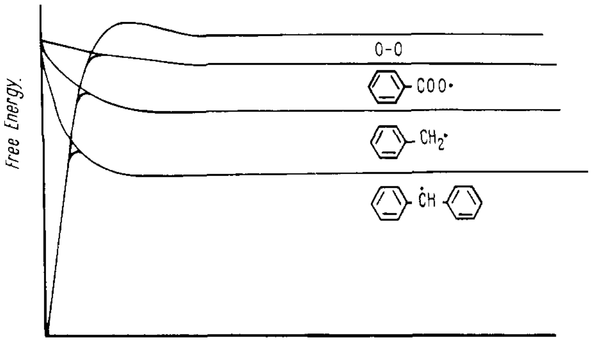

Fig. 1.

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[11] R. Criegee, *Ann.*, **560**, 127 (1948).

Parallel ΔH and ΔS

Figure 2 shows that this series represents another of the increasing number of instances where there is a general relation between enthalpy of activation and entropy of activation in the reaction of a series of compounds. There is a marked tendency for a lowering of the activation energy for perester decomposition to be associated with a lowering of the activation entropy, these effects opposing each other and the net result in this series being in the direction indicated by the enthalpies of activation. Such relations have been observed in a number of kinds of instances[12] and attempts have been made to account for it in rather general terms. It is not, however, invariably found in reactions of homologous or analogous series and it seems worth while in this instance to relate this enthalpy–entropy parallelism as directly as possible to the nature of the process in which it is exhibited.

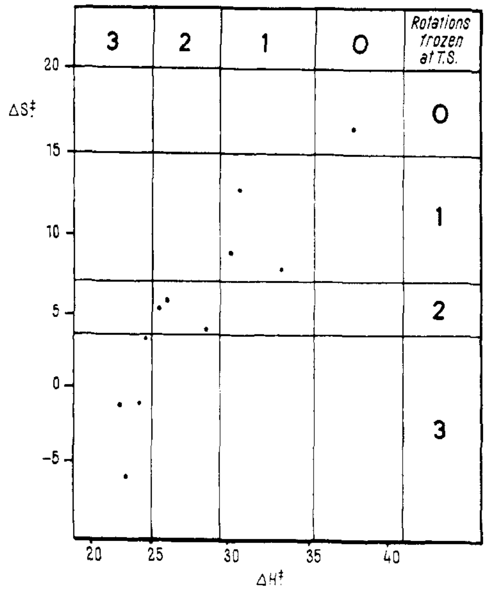

Fig. 2.—$\Delta S^{\ddagger}$ plotted against $\Delta H^{\ddagger}$ for the thermal decomposition of a series of peresters. The rectangles classify the peresters according to the number of bonds whose rotational possibilities become restricted in the transition state for decomposition. The point in the "2" rectangle not reported in Table I is for di-*t*-butyl peroxalate (E. P. Benzing and R. Pincock, unpublished work).

Mechanism of the Relation

If, indeed, partially developed resonance in the dissociation products exists at the transition state and is responsible for a lowering of the energy barrier to reaction, then such resonance will always be at the price of certain steric requirements. For example, if the benzoate radical is more stable than the acetate radical, because of resonance in which the benzene ring is involved, then the activation energy for decomposition of *t*-butyl perbenzoate can be lower than that for *t*-butyl peracetate only if, in the transition state, the carboxylate group and the benzene ring lie in the same plane. This means that many more conformations of *t*-butyl peracetate are acceptable at the transition state than is the case with *t*-butyl perbenzoate. The difference between them, however, is confined to a restricted rotation in one particular bond, the bond between the phenyl group and the carboxylate carbon. Turning to a case of concerted decomposition we recognize that there is also a frozen rotation in the transition state for the decomposition of *t*-butyl trichloroperacetate. Here the carbon–oxygen bond within the carboxylate group must be in a phase of rotation at the transition state which brings the trichloromethyl radical and the *t*-butoxy radical in a relation as nearly *trans* as possible to each other, for the orbitals which are to be used in completing the structure of carbon dioxide must lie in the same plane if any energy is to be realized from this source at the moment of breakdown. By a similar process of reasoning, taking into consideration the nature of the stabilization which can render assistance in the concerted decomposition, each perester of this series can be assigned a number from 0 to 3 corresponding to the number of bonds which may rotate freely in the starting material but which must be in a particular conformation at the transition state. There is now a direct correlation between the amount of lowering realized in the enthalpy of activation (*t*-butyl peracetate being taken as a standard), the number of bonds whose rotation is restricted in the transition state and the lowering of the entropy of activation consequent upon this restriction. *t*-Butyl peracetate with $\Delta S^{\ddagger}$ equal to 17 and a 38-kcal. $\Delta H^{\ddagger}$ has no restricted rotations in the transition state. Three peresters with $\Delta H^{\ddagger}$'s from 33.4 to 30.6 have predicted frozen rotations in one bond each. Their $\Delta S^{\ddagger}$'s lie between 13 and 7.8 entropy units. Three more peresters with $\Delta H^{\ddagger}$'s from 28.7 to 25.5 kcal. need two frozen bonds in the transition state and have $\Delta S^{\ddagger}$ from 5.8 to 3.9, and the four cases with $\Delta H^{\ddagger}$ from 24.7 to 23.0 have three frozen rotations at the transition state and their $\Delta S^{\ddagger}$'s lie between 3.3 and −5.9, three of them being negative. Any actual transition state may be expected to have attained a compromise between a maximal contribution from the resonance energies of the products and a maximal freedom of rotation. In view of the fact then that these numbers of frozen bonds represent simplifications for discussional purposes, it is all the more remarkable that these four classes of peresters lie in mutually exclusive regions as to both enthalpy and entropy of activation. This may well be an example of the general mechanism by which an energy lowering at the transition state can be purchased at the cost of conformational freedom, a situation which will always establish energy–entropy parallelism.

Experimental

Materials. Chlorobenzene.—Chlorobenzene from the Eastman Kodak Co. was shaken with small portions of concentrated sulfuric acid until the acid no longer became colored. The chlorobenzene was washed with water, with a 10% sodium bicarbonate solution, and again with water, dried first over calcium chloride and then over phosphorus pentoxide and distilled through a glass-packed column with 14 theoretical plates. The portion distilling from 130.2–130.5° was used as solvent in the kinetic runs.

Carbon tetrachloride.—Merck reagent grade material was redistilled through a 14-plate column. It boiled at 76.3°.

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[12] J. E. Leffler, *J. Org. Chem.* **20**, 1202 (1955).

***t*-Butyl hydroperoxide**, obtained from the Lucidol Corporation, was given a preliminary drying by the use of a Dean–Stark apparatus[13] at 20 mm. pressure and then distilled at 5 mm. pressure through a 40-cm. column, the pot temperature being below 36°. The fraction boiling at 20.0–20.5 and having $n^{25}D$ 1.3986 was used for preparation of peresters.

Pyridine.—Merck Reagent Grade pyridine was fractionally distilled from barium oxide through a 60-cm. column. For the preparation of all peresters and for kinetic runs with *t*-butyl trifluoroperacetate, the portion distilling at 114–115° was used.

Pentane.—Phillips 66 pentane was used without purification as a solvent in the preparation of peresters. It consistently left no residue on evaporation under aspirator pressure.

Ether.—Technical grade ether was dried with sodium and distilled from it. It boiled at 34–35°.

Synthesis of Peresters.—In general, the peresters were prepared by the slow addition of an excess of *t*-butyl hydroperoxide to an ice-cooled pentane or ether solution of the acid chloride and pyridine. The solution was allowed to stand at −25° until precipitation of pyridinium chloride was complete. The mixture was then poured on ice, washed with cold 10% sulfuric acid to remove excess pyridine, with 10% sodium carbonate and with water. The solution of perester was dried with magnesium sulfate and if no other method of purification was possible, passed down a short chromatographic column packed with Florisil which removed any possible traces of *t*-butyl hydroperoxide remaining. The solvent was then removed under vacuum.

The above procedure was modified in the cases of acetyl, cinnamoyl and 4-phenyl-3-butenoyl chlorides which gave tarry, insoluble complexes with pyridine. The addition was merely reversed, pyridine being added to the solution of acid chloride and hydroperoxide or acid chloride to the solution of pyridine and hydroperoxide. However, the heat evolved in both of these procedures necessitated very efficient cooling of the reaction mixture.

A number of the peresters prepared were oils, thermally unstable and unstable on all but the most non-polar chromatographic media. In such cases, they were purified by removal of excess reactants, the lowest possible temperatures being maintained to minimize thermal decomposition and purity being determined by iodometric titration, infrared spectra and carbon–hydrogen analysis. The titrations were carried out by the method of Simons,[3] the perester being dissolved in a mixture of isopropyl alcohol, acetic acid and acetic anhydride, the solution degassed with small pieces of Dry Ice and allowed to stand with a solution of potassium iodide in a carbon dioxide atmosphere for several hours. The iodine produced was titrated with aqueous sodium thiosulfate to disappearance of the iodine color.

Although this titration method gave concordant results for any one sample, the peroxide analyses were consistently low for peresters of low stability and generally lower than could be reconciled with the carbon–hydrogen analysis. Since unstable peresters and diacyl peroxides tend to be sensitive to acid-catalyzed decomposition, we believe that this method brings about partial decomposition of the unstable peresters and that the infrared spectra and elementary analyses are in these cases more reliable criteria of purity.

The peresters show distinctive infrared spectra. The carbonyl band is lower than that of an ester, usually 0.02–0.03 μ lower than that of the acid chloride. The bands associated with the *t*-butyl group at 3.40, 7.20 and 7.34 μ were always well defined and easily recognized. In purifying peresters for rate determination, special attention was given to freedom of the infrared spectrum from extraneous carbonyl bands and from the OH stretching peak. Different preparations of the same perester conforming to this specification invariably gave the same decomposition rate, indicating that the hydrocarbons, which were the only possible contaminants under these circumstances, were inert. The inertness of the hydrocarbons produced in the perester decomposition was further indicated by the non-autocatalytic nature of the decomposition.

***t*-Butyl Trifluoroperacetate.**—Trifluoroacetic anhydride was prepared in 77% yield, distilling at 38°, lit. 39°, from trifluoroacetic acid by the method of Bourne, Stacey, Tatlow and Tedder[14]; 16 g. of the anhydride, 15 g. of pyridine and 10 g. of *t*-butyl hydroperoxide in 60 ml. of pentane gave 6.1 g. of crude perester containing *t*-butyl trifluoroacetate, a decomposition product. Redistillation gave 3.0 g. of perester boiling at 21° at 22 mm.

***t*-Butyl Peracetate.**—The acetyl chloride was untreated Baker and Adamson material. Acetyl chloride, 4.0 g., *t*-butyl hydroperoxide, 4.0 g., and 5 g. of pyridine gave 2.3 g. of *t*-butyl peracetate, boiling at 22° at 1 mm. The peroxide content by titration was 96.4%.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.54; H, 9.09. Found: C, 55.30, 53.88; H, 9.21, 8.75.

***t*-Butyl α,α-Diphenylperpropionate.**—α,α-Diphenylpropionic acid was prepared from pyruvic acid and benzene by the method of Skerrett and Woodcock.[15] A consistent yield of the desired product of 8% was obtained along with approximately half that much atropic acid. Separation was made by partial acidification of the basic aqueous solution of the two acids and extraction with ether to give almost pure α,α-diphenylpropionic acid. One recrystallization from methanol–water gave a product melting at 173–175°, lit. 174–175°. The acid was refluxed with excess thionyl chloride for 24 hours to give a mixture of acid chloride and anhydride. Additional treatment with thionyl chloride did not appreciably diminish the anhydride content. Distillation of the mixture at 0.2 mm. resulted in partial decomposition of the acid chloride to 1,1-diphenylethylene, determined by infrared, but the distillate contained no anhydride.

This mixture, 2.0 g., with 3.0 g. of *t*-butyl peroxide and 2 g. of pyridine in ether for two days at −25° gave 1.5 g. of a mixture of perester and 1,1-diphenylethylene. Crystallization from pentane gave 0.5 g. of perester, melting at 71–72° dec. The peroxide content by titration was 77.2%.

Anal. Calcd. for $C_{19}H_{22}O_3$: C, 76.51; H, 7.38. Found: C, 76.24; H, 7.29.

***t*-Butyl α-Methyl-α-phenylperpropionate.**—Phenyldimethylcarbinol was made by a Grignard synthesis from phenylmagnesium bromide and acetone. A 73% yield was obtained, distilling 75–76° at 5 mm. Reaction with dry hydrogen chloride and refluxing of the product with methanol for 10 hours gave the methyl ether boiling at 60–63° at 8 mm. This was cleaved by potassium–sodium alloy and carbonated by the method of Ziegler[16,17] to give phenyldimethylacetic acid. The yield from the ether was 77%. Recrystallization from ligroin gave a product melting at 77–78°, lit. 78°.

Refluxing the acid with excess thionyl chloride for 24 hours gave the acid chloride which distilled at 75–77° at 0.2 mm. The acid chloride, 2.5 g., with 5 g. of *t*-butyl hydroperoxide in 1:1 pyridine–ether for 5 days at −25° gave 2.1 g. of an oil which contained an anhydride as well as the desired perester. Chromatography on 20 g. of Florisil with pentane as eluent gave 0.5 g. of the perester containing no anhydride, as determined. The peroxide content by titration was 93.1%.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.19; H, 8.47. Found: C, 71.30; H, 8.67.

***t*-Butyl Percinnamate.**—Cinnamoyl chloride was prepared from Eastman Kodak Co. cinnamic acid by refluxing with a slight excess of thionyl chloride and distilled under reduced pressure. This material, 2.0 g., with 3 g. of *t*-butyl hydroperoxide and 5 g. of pyridine in pentane gave 2.1 g. of *t*-butyl percinnamate, an oil which solidified on standing at −25°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 71.48; H, 7.68.

***t*-Butyl 4-Phenyl-3-perbutenoate.**—4-Phenyl-3-butenoic acid was made by the method of Linstead and Williams[18] in 44% yield, m.p. 87–88°, lit. 87°. The acid chloride was prepared by heating the acid with thionyl chloride at 80° for three hours. The acid chloride, 3.5 g., with 5 g. of *t*-butyl hydroperoxide and 5 g. of pyridine in pentane gave 2.0 g. of an oil which was crystallized from pentane to give

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[13] A. L. Vogel, "A Textbook of Practical Organic Chemistry," second ed., Longmans, Green and Co., New York, N. Y., 1951, p. 340.

[14] E. J. Bourne, M. Stacey, J. C. Tatlow and J. M. Tedder, *J. Chem. Soc.*, 2976 (1949).

[15] E. J. Skerrett and D. Woodcock, *ibid.*, 2806 (1952).

[16] K. Ziegler and B. Schnell, *Ann.*, **437**, 227 (1924).

[17] J. D. Knight and D. J. Cram, THIS JOURNAL, **74**, 5835 (1952).

[18] R. P. Linstead and L. T. D. Williams. *J. Chem. Soc.*, 2375 (1926).

1.3 g. of white crystals melting at 35.5–36° with only slight decomposition. The peroxide content by titration was 81.8%.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.79; H, 7.69. Found: C, 71.90; H, 7.60.

t-Butyl 2-Phenyl-3-perbutenoate.—Gilman's method[19] for the preparation of cinnamylmagnesium chloride and its carbonation gave a 20% yield of 2-phenyl-3-butenoic acid as a colorless oil. Crystallization from pentane at −78° and cold filtration gave a white solid which melted slowly on coming to room temperature (24°); lit.[19] m.p. 23–24°. Heating the acid in a 1:1 benzene–thionyl chloride solution from 40 to 70° over a 3-hour period produced an acid chloride. Reaction of 2.8 g. of this with 5 g. of pyridine and 4 g. of t-butyl hydroperoxide produced 1.8 g. of a yellow oil which gave an infrared spectrum typical of peresters. Decolorization was achieved by passage of a pentane solution of the oil through a small amount of Florisil. The colorless product could not be crystallized and had $n^{25}D$ 1.5066, peroxide content 80.0% by titration.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.79; H, 7.69. Found: C, 72.40; H, 7.91.

Because of the known ease of isomerization of 2-phenyl-3-butenoic acid into the conjugated isomer methylatropic acid, we prepared the latter compound, m.p. 135–136°, and its acid chloride and perester. The infrared spectra showed the two sets of compounds to be different at each stage, the methylatropic acid series having in each case the carbonyl stretching band 0.04–0.05 μ higher than the corresponding member of the unconjugated acid series. t-Butyl 2-phenyl-2-perbutenoate was unchanged by heating at 80° for one hour in carbon tetrachloride, while t-butyl 2-phenyl-3-perbutenoate was completely decomposed.

Procedure of Kinetic Runs.—All runs were carried out in a thermostat controlled to within ±0.01°. A weighed sample of perester was dissolved in a known volume of chlorobenzene, usually 15.00 ml., and the solution transferred to a 25-ml. volumetric flask. This was placed in the constant temperature bath and shaken for two minutes, after which it was clamped in place and a sample transferred by pipet to a test-tube cooled in Dry Ice. This point was considered to be at zero time, and subsequent points were taken after suitable intervals in the same manner.

Of the peresters studied, only t-butyl 4-phenyl-3-perbutenoate decomposed exothermically enough in solution to necessitate stirring or shaking of the flask in which the reaction was carried out.

When temperatures near the boiling point of chlorobenzene were needed to decompose the perester or when other solvents were used, the reaction was run in a series of sealed ampules, all filled with the same solution from a glass manifold.

Points were usually taken up to three or four half-lives, after which the solution was left in the thermostat until complete decomposition had occurred and a final point was taken. This point was considered to be at infinite time and was used as a basis for spectrometric determination of concentrations.

Determination of Relative Concentration of Perester by Infrared.—When all of the samples for a particular run had been obtained, they were warmed to room temperature, uniformly diluted if necessary and the percentage transmission measured for each at the frequency maximum of the perester carbonyl band in the infrared. The instrument used for these determinations was the Perkin–Elmer infrared spectrophotometer model 21. The cells had a 0.4-mm. liquid thickness, and the solvent cell was filled with pure chlorobenzene. After finding the carbonyl maximum, the scanning mechanism was disconnected and the samples viewed in turn. The drum was allowed to move for several minutes with each sample to obtain an average value for the percentage transmission, T_p, theoretically free from random variations in pen position caused by electronic noise. Chlorobenzene, chosen as a solvent in this work for its chemical virtues, was not an ideal solvent for the infrared determinations, since it has five bands in the region 5–6 μ. However, by allowing a sufficient time for equilibration and using chlorobenzene in the solvent cell, T_p could usually be determined with an estimated possible error of ±0.3 in the region of 20–80% transmission, where most of the points were so chosen as to fall. (A concentration of 0.05 M, depending on the relation of the carbonyl band to the chlorobenzene bands, gave a T_p of 20, and reaction to 4 half-lives brought this to about 80.)

From Beer's law it is expected that ($\log T_0 - \log T_p$) will be proportional to the concentration of perester, P, where T_0 is the percentage transmission of solution *vs.* solvent. T_0, however, was not used for the determinations of perester concentration. T_∞, the percentage transmission of the sample taken at infinite time *vs.* pure solvent, was used in its stead. In this manner, complications due to small amounts of products having carbonyl absorption, and general discoloration of the solution with reaction, were avoided. Experimentally, the plots of concentration *vs.* ($\log T_\infty - \log T$) for predetermined mixtures were found to be linear for all but two peresters. These two, t-butyl trifluoroperacetate and t-butyl peracetate, had a linear relation of P to ($\log T_\infty - \log T_p$) up to a value of about 0.5 for the latter, after which concentration increased faster than transmission decreased.

For those peresters where the linear relationship obtained

$$P/P_0 = \frac{(\log T_\infty - \log T_p)}{(\log T_\infty - \log T_p)_0}$$

P_0, the initial concentration of perester, was calculated from the known amounts of perester and solvent used to make up the run. Reaction during the warm-up period of two minutes was assumed to be negligible.

For t-butyl peracetate the results of the kinetic runs were corrected by means of a calibrating graph. For the trifluoroperacetate most of the points were taken in the area of concentration where linearity obtained, and the rates of reaction were taken from the linear portion of the plot of log ($\log T_\infty - \log T_p$) *vs.* time.

For most of the kinetic runs, the graphs of $\log P/P_0$ *vs.* time were straight lines and the first-order rate constants were determined from their slopes. The principal error in the method arises from the dependence of the slope of the line on the transmission at infinite time. A 1% error in the infinity point, easily possible, could change this slope by more than 5%.

In the case of t-butyl 4-phenyl-3-perbutenoate, whose decomposition was not of the first order, plots of $1/P_1^{1/2}$ *vs.* $1/P_2^{1/2}$, where P_1 and P_2 are concentrations of perester in two different runs at different initial concentrations taken after equal time intervals, were very straight lines. From them α was determined by the procedure of Nozaki and Bartlett[20] and then the quantity $\log (\alpha + P^{1/2})/P^{1/2}$ was plotted against time. This plot was rougher, but was used to evaluate the first-order rate constant reported in the table.

Product Studies on Perester Decomposition.—A weighed amount of perester, dissolved in chlorobenzene, was degassed and sealed in a flask under vacuum. It was then heated long enough to ensure complete decomposition and the flask resealed to the vacuum line. The flask containing products and chlorobenzene was cooled with liquid nitrogen and opened to the line by means of a break-seal. The pressure, volume and temperature of the non-condensed gas thus released was noted, and a sample taken for analysis by mass spectroscopy. The cracking pattern obtained using a Consolidated–Nier isotope-ratio mass spectrometer, model 21-201 invariably indicated a mixture of methane and carbon monoxide.

Rough estimates were made of the relative amounts of methane and carbon monoxide, assuming that the concentration ratio was equal to the ratio of intensities of the peaks for mass 15 and mass 28. Calibration of the instrument for each of these gases with respect to helium has justified this approximation.[21] All of the samples measured except that from the trifluoroperacetate decomposition had a ratio of methane to carbon monoxide of about 10 to 1.

After withdrawal of the sample of non-condensable gas, the system was re-evacuated. The remaining products were warmed to room temperature and distilled. The liquid materials were frozen out in the first trap, cooled in Dry Ice–acetone and the gases in the second, cooled by liquid nitrogen. The gases were warmed to room temperature, their pressure and volume noted, the infrared gas cell filled and removed, and the remaining gas tested for absorption on Ascarite.

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(19) H. Gilman and S. A. Harris, THIS JOURNAL, **53**, 3541 (1931).

(20) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 1686 (1946).

(21) Private communication from Mr. K. H. Sauer, Harvard University.

The liquid distillate consisted mainly of chlorobenzene. The presence and quantitative amounts of acetone and *t*-butyl alcohol, which formed the major product from the *t*-butyl group in the free radical decomposition of all the peresters, were determined by infrared spectra in chlorobenzene.

A check of the acetone concentration determined in this manner for the reaction product of *t*-butyl α,α-diphenylperpropionate by the iodine titration method of Messinger[22] gave good agreement. This latter method was employed whenever other materials in the reaction product interfered with the carbonyl band of acetone.

Most of the products from the acid radical of the perester did not distil with the chlorobenzene. This residue was separated into fractions by chromatographing it on acid-washed alumina. The materials thus separated were, for the most part, identified by comparison of their infrared spectra with those of known compounds.

Acknowledgments.—We thank the National Science Foundation for a grant to one of us and a fellowship to the other and the National Institutes of Health for fellowships to the junior author in 1955 and 1956.

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[22] F. Wild, "Estimation of Organic Compounds," Cambridge University Press Cambridge, England, 1953, p. 165.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW MEXICO]

The Synthesis of 5,8-Dimethyl-3,4-benzpyrene, 5,10-Dimethyl-3,4-benzpyrene and 5,8,10-Trimethyl-3,4-benzpyrene[1,2]

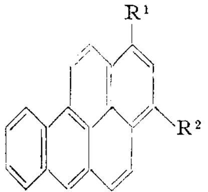
BY JULES L. ADELFANG[3] AND GUIDO H. DAUB

RECEIVED OCTOBER 24, 1957

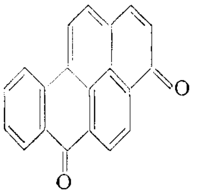
The substituted malonic ester obtained from the condensation of 10-chloromethyl-9-methylanthracene (V) with diethyl malonate was hydrolyzed and decarboxylated providing β-(10-methyl-9-anthranyl)-propionic acid (VI) in 64% yield from V. The synthesis of VI was also accomplished in 85% yield by stannous chloride reduction of β-(10-iodomethyl-9-anthranyl)-propionic acid prepared by iodomethylation of β-(9-anthranyl)-propionic acid. Reduction of the acid VI with sodium in boiling *n*-amyl alcohol afforded β-(10-methyl-9,10-dihydro-9-anthranyl)-propionic acid which upon cyclization produced 3-keto-7-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthracene (X). The Stobbe condensation with the ketone X gave β-carbethoxy-β-(7-methyl-1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XI) in 85% yield. The half-ester XI was decarbethoxylated providing β-(7-methyl-1,11b-dihydro-7H-*meso*-benzanthrenyl-3)-propionic acid (XII). Reduction of the acid XII produced β-(7-methyl-1,2,3,11b-tetrahydro-7H-*meso*-benzanthrenyl-3)-propionic acid which was cyclized to 8-keto-5-methyl-1,2,2a,5,8,9,10,10a-octahydro-3,4-benzpyrene (XVI). The ketone XVI was treated with methylmagnesium iodide producing a carbinol which was dehydrated and dehydrogenated to 5,8-dimethyl-3,4-benzpyrene (XVII). The hydrocarbon XVII was identical with the compound isolated from Wolff–Kishner reduction of 8-methyl-3,4-benzpyrene-5-aldehyde (XIX) which was obtained by formylation of 8-methyl-3,4-benzpyrene. Cyclization of the half-ester XI provided 10-carbethoxy-8-keto-5-methyl-1,2,8,9,10,10a-hexahydro-3,4-benzpyrene (XX) in 35% yield. The ketone XX was reduced with lithium aluminum hydride and the resulting diol was dehydrated and dehydrogenated producing 5,10-dimethyl-3,4-benzpyrene in 25% yield from XX. Formylation of 8,10-dimethyl-3,4-benzpyrene (XXIII) with N-methylformanilide afforded 8,10-dimethyl-3,4-benzpyrene-5-aldehyde which was directly reduced by the Wolff–Kishner method producing 5,8,10-trimethyl-3,4-benzpyrene in 25% yield from XIX.

Carcinogenic testing has shown that the 5-,[4] 8-,[5] and 10-monomethyl-3,4-benzpyrenes[5] and 8,10-dimethyl-3,4-benzpyrene[5] are quite active. The synthesis of the remaining 3,4-benzpyrenes having methyl groups in the 5-, 8- and 10-positions, namely the 5,8-dimethyl-, 5,10-dimethyl- and 5,8,10-trimethyl-3,4-benzpyrenes, is presented here.

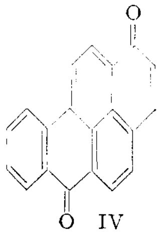
These compounds are of interest since it has been demonstrated that mice will metabolize 3,4-benzpyrene to non-carcinogenic oxidized products involving the 5-, 8- and 10-positions. Wiegert and Mottram[6] found that the main metabolite obtained from the feces of mice given intravenous injections of 3,4-benzpyrene was 8-hydroxy-3,4-benzpyrene (I). Berenblum and Schoental[7] also found 8-hydroxy-3,4-benzpyrene along with 10-hydroxy-3,4-benzpyrene (II), 3,4-benzpyrene-5,8-quinone (III), and 3,4-benzpyrene-5,10-quinone (IV) in the feces of rats given intraperitoneal injections of 3,4-benzpyrene.



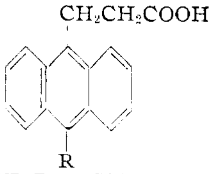
I, $R^1 = H, R^2 = OH$
II, $R^1 = OH, R^2 = H$



III



IV



VI, $R = CH_3$
VII, $R = H$
VIII, $R = CH_2I$

The synthesis of 5,8-dimethyl-3,4-benzpyrene (XVII) and 5,10-dimethyl-3,4-benzpyrene (XXII) was accomplished from β-(10-methyl-9-anthranyl)-propionic acid (VI), an intermediate readily available from anthrone. 9-Methylanthracene, prepared by treatment of anthrone with methylmag-

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[1] From the dissertation presented by Jules L. Adelfang to the graduate faculty of the University of New Mexico in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] This investigation was supported in part by a research grant (C-1595) from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

[3] Graduate Research Assistant, February, 1956, to August, 1957.

[4] L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **60**, 2542 (1938).

[5] D. W. Stanger, Northwestern University Medical School, unpublished results.

[6] F. Wiegert and J. C. Mottram, *Cancer Research*, **6**, 97 (1946).

[7] I. Berenblum and R. Schoental, *ibid.*, **6**, 699 (1946).