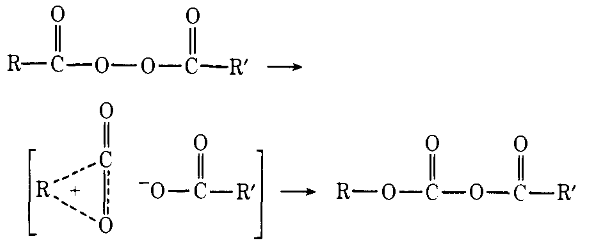
Decomposition of Bicyclo[2.2.2]-1-formyl and Pivaloyl Peroxides

J. E. Leffler* and A. A. More

Contribution from the Department of Chemistry, Florida State University, Tallahassee, Florida 32306. *Received May 28, 1971*

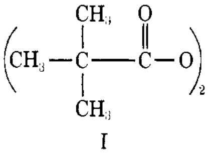
Abstract: Pivaloyl peroxide (I) decomposes in CCl_4 *at 10°* with a rate constant of 1.9×10^{-4} sec^{-1} while bicyclo[2.2.2]octane-1-formyl peroxide (II) decomposes in CCl_4 *at 30°* with a rate constant of 1.71×10^{-4} sec^{-1}. Both peroxides are less stable than isobutyryl peroxide. The decomposition of II is accelerated by carboxylic acid catalysts and by polar solvents, the acid catalysts obeying a Brønsted relationship with $\alpha = 0.52$ in CCl_4. The thermal decomposition of II in CCl_4 gives a mixture of typical radical and ion-pair or carboxy-inversion products, the proportion of the latter increasing in the presence of trichloroacetic acid catalyst. Photolysis of II in CCl_4 gives none of the ionic reaction products. The thermal decomposition of I in CCl_4 also gives both radical product (*tert*-butyl chloride) and ion-pair products (*tert*-butyl pivalate, pivalic acid, and isobutylene). Walling's proposal of a common intermediate for the radical and ionic products is discussed and a modified structure is suggested for the intermediate.

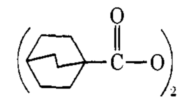
The carboxy-inversion reaction of diacyl peroxides, an alternative to the more extensively studied decomposition into free radicals, was discovered by applying the principle that reactions leading to ions are more sensitive to polar substituents and polar solvents than are radical reactions[1]


(1)

The decomposition of benzoyl peroxide in benzene gives products that appear to derive exclusively from radical intermediates, while the decomposition of *p*-methoxy-*p′*-nitrobenzoyl peroxide in polar solvents gives products that appear to derive largely from ion-pair intermediates. *Assuming that the two modes of reaction are independent*, the product ratios can be used to obtain the separate rate constants for the disappearance of the peroxide. On this basis $k_{\text{ion pair}}$ is greatly increased by the introduction of *p*-methoxy-*p′*-nitro substituents and by the shift from benzene to nitrobenzene as solvent, while k_{radical} changes in a less predictable way and by less than an order of magnitude.

However, it is now known that some *symmetrical* diacyl peroxides also give a considerable proportion of polar reaction products.[2,3] The reaction appears to be general for diacyl peroxides with a weak carbon to carboxyl bond, including phenylacetyl peroxide, secondary aliphatic diacyl peroxides, tertiary aliphatic diacyl peroxides, and even peroxides with the functional group at a bridgehead.[4-6] In this paper we present evidence that pivaloyl peroxide (I) and bicylo[2.2.2]-octane-1-formyl peroxide (II) also give the ionic reaction.[7]


I


II

Bis(bicyclo[2.2.2]octane-1-formyl) Peroxide. Bis(bicyclo[2.2.2]octane-1-formyl) peroxide (II) decomposes at a convenient rate ($k = 17.1 \times 10^{-5}$ sec^{-1}) in CCl_4 at 30°. The reaction is quite accurately first order and the rate constants are insensitive to changes in initial concentration over a range from 0.01 to 0.1 *M*.

Medium Effects and Acid Catalysis. Table I shows the values of the first-order rate constant in a series of solvents listed in order of increasing dielectric constant.

Table I. Effect of Solvent Changes and Catalysts on the Rates of Decomposition of Bicyclo[2.2.2]octane-1-formyl Peroxide

Solvent effects[a]	10^5k_1, sec^{-1}	Catalytic effects[b]	10^5k_1, sec^{-1}
Isooctane	5.0	0.019 *M* CH_3COOH	16.8
Cyclohexane	6.1	0.0189 *M* $ClCH_2CH_2COOH$	20.3
Carbon tetrachloride	17.1	0.0117 *M* $ClCH_2COOH$	26.5
Toluene	36.6	0.0215 *M* $Cl_2CHCOOH$	66.2
Chlorobenzene	62.0	0.0206 *M* Cl_3CCOOH	173

[a] No catalyst unless otherwise noted. [b] In CCl_4.

To the extent that it has been investigated, diacyl peroxides that decompose to polar products are also sensitive to acid catalysis and follow Brønsted linear free energy relationships.[1,8] Figure 1 and Table I

---

[1] J. E. Leffler, *J. Amer. Chem. Soc.*, **72**, 67 (1950).

[2] F. D. Greene, H. P. Stein, C.-C. Chu, and F. M. Vane, *ibid.*, **86**, 2080 (1964).

[3] C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiaonnou, *ibid.*, **92**, 4927 (1970).

[4] P. D. Bartlett and F. D. Greene, *ibid.*, **76**, 1088 (1954).

[5] (a) M. S. Kharasch, F. Engelmann, and W. H. Urry, *ibid.*, **65**, 2428 (1953); (b) W. F. Sager, Thesis, Harvard University, 1948.

[6] In some cases the evidence for the ionic reaction is actual isolation of the carboxy-inversion product and in others the spectroscopic detection of that substance as a transient intermediate. Some of the earlier literature, in which large yields of ester were reported, has been reinterpreted in terms of carboxy-inversion reactions or related ion-pair reactions rather than radical cage processes.[3]

[7] A. A. More, Dissertation, Florida State University, 1970.

[8] P. D. Bartlett and J. E. Leffler, *J. Amer. Chem. Soc.*, **72**, 3030 (1950).

Table II. Products from the Decomposition of Bicyclo[2.2.2]octane-1-formyl Peroxide in Carbon Tetrachloride[a,b]

$[P]_0$[c]	RCl	ROH	RCOOH[d]	RCOOR	CCl_3CCl_3
0.0333[e]	17.7	14.4	12.7	88.6	8.3
0.0373[e]	18.6	15.7	12.4	81.8	5.6
0.0319[f]	19.1	75.1	68.2	15.6	5.4
0.0373[f]	18.2	75.1	70.7	14.8	7.4
0.0280[g]	42.2	0.0	30.1	0.0	88.8
0.0249[g]	43.1	0.0	30.2	0.0	88.3
0.0269[e,h]	2.7	20.6	39.6	62.9[i]	

[a] Yields are in mol %/mol of peroxide (±3%). [b] R is bicyclo[2.2.2]-1-octyl. [c] Initial peroxide concentration. [d] The acid formed in the reaction was converted to the methyl ester by means of diazomethane. [e] The decomposition was carried out at 30.0° for 12 hr, then 126.7° for 1 week. [f] The ampoules contained 1 ml of water. After 12 hr at 30.0°, the ampoules were heated at 80.0° for 1 week. [g] The peroxide was decomposed with 3500-Å light at −5°, 0.0373 *M* benzophenone as sensitizer. [h] Acid-catalyzed, 0.0270 *M* initial [Cl_3CCOOH]. [i] Bicyclo[2.2.2]-1-octyl trichloroacetate was also formed, 26.0 mol %/mol of peroxide.

show the effect of equimolar amounts of several acids on the first-order decomposition of bicyclo[2.2.2]-octane-1-formyl peroxide in CCl_4 at 30°. Acetic acid, the weakest tried, had no effect at 0.02 *M*.

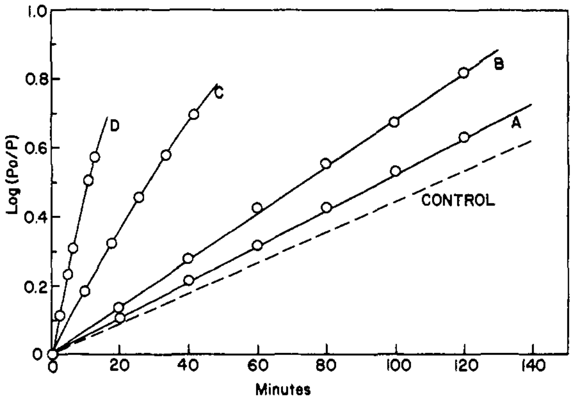


Figure 1. Effect of added acids on the decomposition of bicyclo-[2.2.2]octane-1-formyl peroxide in CCl_4 at 30°. Dotted line represents typical runs without added acid. In the runs with added acid the initial concentrations of peroxide and acid were equal: (A) 0.0189 *M* β-chloropropionic acid, (B) 0.0116 *M* chloroacetic acid, (C) 0.021 *M* dichloroacetic acid, (D) 0.020 *M* trichloroacetic acid. Acetic acid, both concentrations 0.02 *M*, had no measurable effect.

If straight lines are fitted to the somewhat curved plots of Figure 1, the resulting slopes can be used to obtain catalysis constants, k_a, for the various acids. Figure 2 shows the Brønsted plot of log k_a against pK_a *(water)* of the acids. The slope, α, is 0.52.

The downward curvature apparent in the plots for the acid-catalyzed reactions is probably real and due to the progressive replacement of strong acid by the much weaker, and probably totally ineffective, bicyclo-[2.2.2]octane-1-carboxylic acid. Unfortunately the data are not precise enough to permit an accurate estimate of the catalyst consumption, although it appears to be a considerable fraction of the peroxide decomposed in the catalyzed part of the reaction.

Thermal Decomposition Products. In damp[9] carbon tetrachloride at 30° the products (Table II) of the *thermal* decomposition of 0.03 *M* bicyclo[2.2.2]octane-1-formyl peroxide are hexachloroethane and 1-chlorobicyclo[2.2.2]octane in low yield, the alcohol 1-hydroxybicyclo[2.2.2]octane, its ester with bicyclo[2.2.2]octane-1-carboxylic acid, and the acid itself. The usual carboxy-inversion product was also formed, as indicated by the infrared spectrum, although we were unable to isolate it. Heating the reaction mixture after the initial decomposition at 30° converted the carboxy-inversion intermediate to CO_2 and the ester; reaction in the presence of deliberately added water, followed by heating, either diverted the ion pair or converted the carboxy-inversion product to alcohol and acid rather than ester.

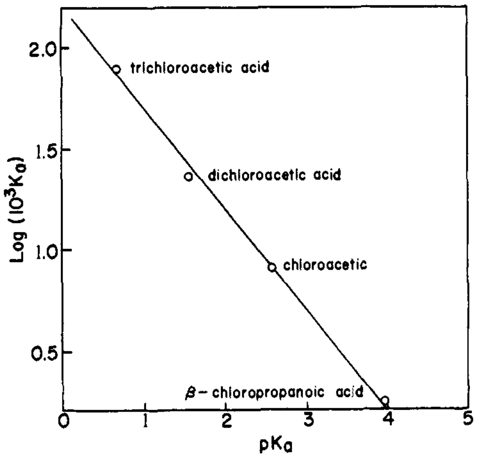


Figure 2. Brønsted catalysis plot for bicyclo[2.2.2]octane-1-formyl peroxide in CCl_4 at 30°.

Photolysis Products. Photolysis in the presence of benzophenone gave the alkyl chloride, hexachloroethane, and acid, but no alcohol or ester (Table II). A control experiment showed that the carboxy-inversion product does not photolyze appreciably under the same conditions.

Acid-Catalyzed Products. Added trichloroacetic acid (Table II) greatly reduces the yield of radical products and, after decomposition of carboxy-inversion compound, gives two esters, the usual ester and bicyclo-[2.2.2]-1-octyl trichloroacetate. The yields of alcohol and bicyclo[2.2.2]-1-formic acid are also increased. Control experiments showed that the trichloroacetate ester is not formed by reaction of the carboxy-inversion product or the ester with trichloroacetic acid at 127°. Some trichloroacetate is produced by heating the alcohol and trichloroacetic acid.

Pivaloyl Peroxide. The first-order rate constant for the decomposition of pivaloyl peroxide in CCl_4 at 10°

---

[9] The solid peroxide and its solutions are too unstable to permit the use of elaborate drying procedures.

Table III. Products from the Decomposition of Pivaloyl Peroxide in CCl_4 at 10°

Product	Yield, $M \times 10^3$	Product	Yield, $M \times 10^3$
tert-Butyl chloride	14.7	pivalic acid	67.0
tert-Butyl alcohol	4.0	isobutane	(3.6)[a]
tert-Butyl pivalate	33.3	isobutylene	(18.6)[a]

[a] Most of the gaseous product was lost, but the amount of isobutylene is significantly greater than the amount of isobutane.

is about 19 × 10^{-5} sec^{-1}. The reaction products (Table III) are listed with their yields as moles per liter of product solution, rather than mole per cent, because this peroxide is too unstable in the solid state to permit weighing. The infrared spectrum of the freshly decomposed peroxide solution in CCl_4 again shows bands indicative of a carboxy-inversion intermediate. The carbonyl doublet due to the peroxide (1798 and 1775 cm^{-1}) is succeeded by new bands at 1804 and 1760 cm^{-1}. These bands in turn disappear on heating at 127°, to be succeeded by a carbonyl peak at 1724 cm^{-1}. The bands at 1804 and 1760 cm^{-1} were assigned to the carboxy-inversion product on the basis of the spectrum of a synthetic sample.

Discussion

In many instances the substituent effects on the decomposition of diacyl peroxides fit the model of kinetically independent radical and ion-pair processes quite well, the rate constant for the radical reaction being relatively insensitive to purely polar effects and the rate constant for the ion-pair reaction undergoing large changes. In the case of α branching of the diacyl peroxide, both reactions are accelerated by the substituent, which is reasonable if the alkyl to carboxyl bond has been weakened in both transition states. Thus for both the ion-pair and radical reactions it is plausible that tertiary diacyl peroxides are less stable than secondary, that a bridgehead location for the functional group increases the stability, and that the bicyclo[2.2.2]-octane bridgehead compound is less stable than the bicyclo[2.2.1]heptane bridgehead compound, as shown in Table IV. The observed sequence of reactivity is the same as that for the solvolysis of the corresponding series of alkyl bromides (*tert*-butyl bromide, bicyclo[2.2.2]-1-octyl bromide, etc.)[10] and nearly the same as the sequence of rate constants for decarbonylation of the corresponding acyl radicals.[11,12] In the decomposition of a series of isobutyryl benzoyl peroxides with substituents in the benzoyloxy moiety, the apparent k_{radical} as measured by the yield of scavengeable radicals, has the entirely reasonable Hammett ρ value of -0.10 and the total rate constant a ρ of $+0.90$.[13]

Table IV. Comparison of Decomposition Rates and Temperatures

	Peroxide, solvent				
	Pivaloyl, CCl_4	Bicyclo-[2.2.2]-octane-1-formyl, CCl_4	Isobutyryl,[3] C_6H_6	Apocamphane-1-formyl,[5] C_6H_6	Triptoyl,[4] C_6H_6
10^4k, sec^{-1}	1.9	1.71	2.4	2.3	1.4
T, °C	10	30	40	80	80
% polar reaction	85[a]	91[b]	30[c]	50[d]	41[e]

[a] From yields of ester, acid, and alcohol and assuming that an ion-pair reaction leads to isobutylene plus pivalic acid. [b] 100% − yield RCl/2. Yield of ester was 85%. [c] Carboxy-inversion product. Ester also reported, 11.5%.[3] [d] Ester. [e] Ester plus alcohol.

However, there are other instances of structural and solvent effects on the apparent k_{radical} and $k_{\text{ion pair}}$ that are more difficult to rationalize. In the decomposition of isobutyryl peroxide, for example, polar solvents increase both k_{radical} and $k_{\text{ion pair}}$, so that it is necessary to assume that the transition state for the radical reaction is almost as polar as that for the ion-pair reaction. Also, the substitution of a benzoyloxy moiety for one of the isobutyryloxy moieties, in cyclohexane solvent, appears to just double $k_{\text{ion pair}}$ while decreasing k_{radical} by perhaps two orders of magnitude. Hence, the transition state for the radical reaction has to be stabilized to a disproportionate extent by the presence of two weak carbon-to-carboxy bonds rather than just one such bond. Rather than accept these *ad hoc* explanations, Walling[3] has proposed that the two reactions share a common rate-determining transition state and a common first intermediate (which he identifies as an intimate ion pair) and then diverge to ionic and radical products.[14] The ion pair can either react to give polar products or separate to give fragments loosely enough coupled to be considered a *radical* pair.

Although the present authors are attracted by a proposal that the reaction path branches at a common intermediate, we have some reservations about the nature of that intermediate and particularly about the suggested *reversible* interconversion of the ion pairs and radical pairs. One objection to the reversible interconversion is that CIDNP[15] signals are usually detectable in the apparently radical products but are absent in the products assigned to the ion-pair reaction,[16a] which might make it doubtful that the intermediates leading to ionic products have ever been part of the radical pair population.[16b]

The observation of exclusively radical products[17-19]

---

(10) F. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(11) D. E. Applequist and L. Kaplan, *J. Amer. Chem. Soc.*, **87**, 2194 (1965).

(12) The relative rate constants for the decarbonylation reaction were obtained by competition between decarbonylation and acid chloride formation, neglecting any substituent effect on the chlorine abstraction reaction.[11] The single difference in the two sequences is that pivaloyl reacts faster than bicyclooctane-1-formyl in the peroxide series but appears to react more slowly in the acyl-radical decarbonylation series.

(13) R. C. Lamb and John R. Sanderson, *J. Amer. Chem. Soc.*, **91**, 5034 (1969).

(14) Branching of a reaction path probably has to occur at an *intermediate* rather than at a transition state or immediately after a transition state: (a) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1970, p 157; (b) J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.*, **64**, 371 (1968); (c) R. N. Porter, D. L. Thompson, L. B. Sims, and L. M. Raff, *J. Amer. Chem. Soc.*, **92**, 3208 (1970); (d) J. E. Leffler and R. D. Temple, *ibid.*, **89**, 5235 (1967).

(15) Chemically induced dynamic nuclear polarization.

(16) (a) C. Walling and A. R. Lepley, *ibid.*, **93**, 546 (1971). (b) Strictly speaking this argument applies only to interconversion of radical and ion pairs in which at least one of the radicals has decarboxylated. The nuclear polarization of protons in an acyloxy radical, as opposed to an alkyl radical, is likely to be very small.

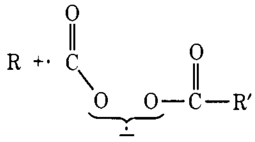
(17) (a) C. Walling and M. J. Gibian, *ibid.*, **87**, 3413 (1965); (b) unpublished observations, this laboratory.

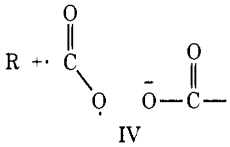
(18) J. E. Leffler and R. Zepp, *ibid.*, **92**, 3713 (1970).

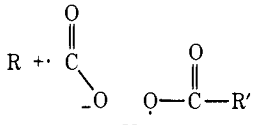
(19) Although a small yield of carboxy-inversion product was re-

from the photolysis, as opposed to the thermolysis, of diacyl peroxides also requires some adjustment of the theory. Photolysis, at least with light of moderate frequencies, produces acyloxy radical pairs, probably identical with those produced in thermal reactions. They can be prevented from decarboxylating, for example, by the presence of reactive hydrogen-donor solvents. If acyloxy radical and ion-pair intermediates are interconvertible in both directions, photochemical carboxy-inversion reactions should occur.

If there is indeed a common intermediate we would suggest that it is formed by single electron transfer from the weak carbon–carbon two-electron bond to the peroxide linkage, and that it can be represented by III. Intermediate III is electronically a singlet and the alkyl and carbon dioxide groups are still weakly bonded although the bonding orbital is only singly occupied. In III, the two acyloxy moieties have unequal RCOO· and RCOO$^-$ characteristics. Suitable polar substituents, and polar solvents, would favor canonical structure IV and promote conversion to the ion pair of eq 1. Less polar solvents or less suitable substituents favor canonical structure V, which is less highly polarized, and promote (irreversible) conversion to an acyloxy radical pair. The charge distribution in the rate-determining transition state preceding III would be compatible with the observed substituent, medium, and structural effects, including the effect of α-alkyl substituents and bridgehead structures. The internal single electron transfer is also closely analogous to mechanisms involving transfer of an electron from an external reagent that have been postulated for the reaction of diacyl peroxides with triphenylphosphine or amines and for other "molecule assisted" and neighboring group assisted homolyses.


III


IV


V

Experimental Section[7]

Methyl 1,3-Cyclohexadiene-1-carboxylate. This compound was prepared from crotonaldehyde *via* 1-acetoxybutadiene and methyl 2-acetoxy-Δ^3-cyclohexene-1-carboxylate.[20]

Ethyl 1,3-Cyclohexadiene-1-carboxylate. This compound was prepared from crotonaldehyde *via* 1-(diethylamino)-1,3-butadiene and ethyl 2-(diethylamino)-Δ^3-cyclohexene-1-carboxylate.[21]

Ethyl Bicyclo[2.2.2]oct-2-ene-1-carboxylate. A 400-ml silver-lined steel autoclave equipped for shaking[22] was charged with 49 g of ethyl 1,3-cyclohexadiene-1-carboxylate in 50 ml of benzene. The vessel was evacuated and filled with ethylene gas. The autoclave was heated at 160° and ethylene was injected at a pressure of 3000 atm, until no further pressure drop occurred (14 hr). The autoclave was cooled and the ethylene was vented. The solution was removed and vacuum distilled, to yield 29.8 g (51%) of colorless methyl bicyclo[2.2.2]octa-2-ene-1-carboxylate, bp 104–106° (13 mm) [lit.[21] 95–100° (11 mm)].

Methyl Bicyclo[2.2.2]oct-2-ene-1-carboxylate.[22] The same procedure as described above for the ethyl ester was used for the methyl ester. The boiling point of methyl bicyclo[2.2.2]octa-2-ene-1-carboxylate is 96° (9 mm).

Methyl and Ethyl Bicyclo[2.2.2]octane-1-carboxylates. The unsaturated ester (16 g) was hydrogenated at low pressure in 75 ml of 95% alcohol, using 200 mg of platinum oxide (2 hr). After filtration and stripping of the solvent, the saturated methyl ester was distilled, bp 81–82° (8 mm). The saturated ethyl ester, bp 101–103° (12 mm), lit.[21] 96–98° (12 mm), was prepared in the same way.

Bicyclo[2.2.2]octane-1-carboxylic Acid. The acid, mp 140–142°,[21] was obtained *via* hydrolysis of either of the two esters with aqueous–alcoholic KOH.

1-Bromobicyclo[2.2.2]octane. This compound was prepared from the acid by reaction with HgO and Br_2.[23]

1-Hydroxybicyclo[2.2.2]octane. This compound was prepared from the bromide by hydrolysis with $CaCO_3$ and aqueous dioxane in a sealed tube at 130°.[21]

1-Chlorobicyclo[2.2.2]octane. This compound was prepared from the alcohol by reaction with $ZnCl_2$ and HCl.[20] Direct reaction from the bromide gave a product that still contained some of the starting material as an impurity.

Bicyclo[2.2.2]-1-octyl Bicyclo[2.2.2]octane-1-carboxylate. Bicyclo[2.2.2]octane-1-carboxylic acid, 1.0 g (0.0065 mol), and red mercuric oxide, 1.0 g (0.0046 mol), were placed in a 50-ml three-neck flasked equipped with a condenser, a solid addition funnel, and a magnetic stirrer. Solvent, 25 ml of cyclohexane dried over sodium, was added to the solids and the mixture heated to 80° while stirring vigorously. Iodine, 1.5 g (0.0063 mol), sublimed from phosphorus pentoxide, was added slowly over a period of 1 hr. When the addition was complete, the reaction mixture was heated for an additional hour, cooled to room temperature, and filtered. Unreacted acid was extracted with 1 *N* potassium hydroxide. The solution was then dried over Drierite and concentrated to about 2 ml by careful fractionation, and low melting by-product was removed by sublimation at 60° (18 mm). The residue was purified by chromatography on Florisil, yield 33%. This ester softens at 104°, mp 108.5–110.5° (lit.[23] 88.5–89.5°).

Because of the discrepancy in melting points, the ester was also synthesized from 1-hydroxybicyclo[2.2.2]octane, bicyclo[2.2.2]octane-1-carbonyl chloride, and pyridine. The product of this reaction had the same glc retention time and infrared spectrum as the material synthesized by the first procedure.

Bicyclo[2.2.2]octyl-1 Trichloroacetate. Trichloroacetic acid, 0.066 g (4.1×10^{-4} mol), was added dropwise to a mixture of 1-hydroxybicyclo[2.2.2]octane, 0.0284 g (2.26×10^{-4} mol), 5 ml of pentane, and pyridine, 0.066 g (8×10^{-4} mol). After stirring for 12 hr and filtering, the filtrate and pentane washings were concentrated, excess pyridine removed *in vacuo*, and the solid residue chromatographed in pentane on Florisil. The eluted solid was sublimed at 50° (2 mm) to give 0.034 g of the desired ester, mp 69.5–71.5°, strong infrared bands at 1760, 1239, and 1017 cm^{-1}.

Bicyclo[2.2.2]octane-1-carbonyl Chloride. Bicyclo[2.2.2]octane-1-carboxylic acid (6 g) was dissolved in thionyl chloride and left overnight. The excess thionyl chloride was removed on a rotary evaporator and the residue vacuum distilled to give 5.0 g of the chloride, bp 68° (0.8 mm).

Bicyclo[2.2.2]octane-1-formyl Peroxide. The procedure described below is essentially that of Silbert and Swern.[24] This reaction was run in a cold room (temperature 3°) to prevent decompositon of the peroxide. Unless otherwise noted, all apparatus and solvents were at the cold-room temperature.

A mixture of 25 ml of ether, 1.0 g of bicyclo[2.2.2]octane-1-carbonyl chloride, and 0.6 g of pyridine was precooled to −15°, and then 0.83 g of 60% H_2O_2 was added with stirring in the course of 1 hr. The solution was stirred at 0° for an additional 2 hr, diluted with a further 25 ml of ether, and washed with three 50-ml portions of 1 *N* HCl, three 50-ml portions of 1 *N* NaOH,[25] and three 50-ml

---

ported for a photolysis in ref 3, the experiment was conducted at a temperature at which competing thermolysis could not be neglected.

[20] A. A-R. Sayigh, Dissertation, Columbia University, 1952.

[21] C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

[22] The authors thank E. I. duPont de Nemours and Co., and especially Dr. L. J. Story, Dr. J. C. Kauer, and Mr. W. P. Branch for graciously consenting to run this reaction at their high-pressure laboratory.

[23] F. W. Baker, H. D. Holtz, and L. M. Stock, *J. Org. Chem.*, **28**, 514 (1963).

[24] L. S. Silbert and D. Swern, *J. Amer. Chem. Soc.*, **81**, 2364 (1959).

[25] Failure to wash with strong alkali causes the product to contain substantial amounts of bicyclooctanepercarboxylic acid, which is quite stable.

portions of water. After drying over $MgSO_4$, the ether was removed under reduced pressure at temperatures not exceeding 0°. The white solid residue was then crystallized by dissolving it in pentane at 0°, cooling in liquid N_2, and quickly filtering out the crystalline peroxide. Traces of solvent were removed by pumping at 10^{-6} mm and 0° for 1 hr. The solid was then weighed (in the cold room) and dissolved in CCl_4 (or other solvent) at 0°. The iodometric assay of the peroxide prepared in this way is 93–96%.

Pivaloyl Peroxide. This compound was prepared by the method of Kochi and Mocadlo.[26] The solid peroxide was dissolved in CCl_4 without weighing and used immediately. *Caution:* A sample of the solid peroxide detonated during an attempt to weigh it at 3°.

Iodometric Titrations. To an aliquot of the peroxide solution is added 25 ml of acetone (saturated with O_2) and then a saturated *clear colorless* solution of NaI in 3 ml of carbonated acetone. The mixture is stored for 30 min in the dark, then diluted with 150 ml of carbonated water, and titrated with thiosulfate to a starch–iodine end point, with stirring.

Trimethylacetic *tert*-Butylcarbonic Anhydride. This carboxy-inversion product was synthesized by the general method of Michejda and Tarbell,[27] and characterized by its infrared bands at 1804 and 1760 cm^{-1}.

Adamantane-1-formyl Peroxide. In an attempted preparation of this peroxide by the method used for pivaloyl peroxide, the solid produced was found to be devoid of oxidizing power.[28]

Acknowledgment. The authors wish to thank Professor J. Saltiel and his collaborators for many helpful discussions. Financial support of this research by the Chemistry Programs, National Science Foundation Grants No. GP 8015 and GP 15991, is gratefully acknowledged.

---

[26] J. K. Kochi and P. E. Mocadlo, *J. Org. Chem.*, 30, 1134 (1965).

[27] C. J. Michejda and S. Tarbell, *ibid.*, 29, 1168 (1964).

[28] The products of an attempted preparation are reported to be the alcohol, acid, and ester, indicating a rapid ionic decomposition: L. F. Fieser, M. Z. Nazer, S. Archer, D. A. Berberian, and R. G. Slighter, *J. Med. Chem.*, 10, 517 (1967).

Thermal Isomerization of Substituted Allylpyrroles

John M. Patterson,* Jan W. de Haan,[1] Michael R. Boyd, and J. Douglas Ferry

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506. *Received June 25, 1970*

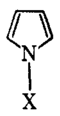
Abstract: *N*-(Substituted allyl)pyrroles, where the substituted allyl group is α-methylallyl, *trans*-crotyl, and *cis*-crotyl, on thermolysis isomerize to the corresponding 2-substituted pyrroles without rearrangement of the migrating allyl group and to the 3-substituted pyrroles with inversion of the allyl group. Since the reactions were found to be first order and intramolecular, these results are regarded as evidence for competing [1,5] and [3,3] sigmatropic shifts, respectively. Activation parameters for these reactions are consistent with this viewpoint. The interconversion of 2- and 3-(substituted allyl)pyrroles probably involves competing [1,5] and [3,3] sigmatropic shifts as well. The thermolysis of *N*-(substituted allyl)-2,5-dimethylpyrroles produces a mixture of inverted and noninverted 3-(substituted allyl)-2,5-dimethylpyrroles.

Alkyl and benzyl substituents in the pyrrole molecule upon heating migrate irreversibly from the N to the 2 position and reversibly from the 2 to 3 position.[2–4] Similar migrations in which the 2 and 5 positions of the pyrrole ring are blocked probably proceed through 2,2-dialkyl-2*H*-pyrrole (α-pyrrolenine) intermediates.[4] The values of the activation parameters[2,3] and the fact that the migrations occur with a large degree of retention of configuration[5] indicate that these reactions might involve thermal [1,5] sigmatropic shifts of allyl groups similar to those observed in alkyl-substituted cyclopentadienes.[6]

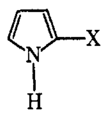
Inversion of the allyl group is characteristic of the Claisen or Cope rearrangement[7] and such rearrangements of the amino-Claisen type have been reported[8] recently in the isoxazolinone and pyrazolinone series. Most quantitative information about Claisen shifts (kinetic parameters and product production) has been obtained from solution studies,[9] and only limited information is available from rearrangements carried out in the gas phase. This report is concerned with the thermal behavior of (substituted allyl)pyrroles in the gas phase.

Results

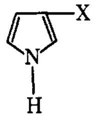
Compounds I–IV, where X refers to a substituted allyl group such as α-methylallyl (a), *trans*-crotyl (b), and *cis*-crotyl (c), were pyrolyzed in a gas-phase flow



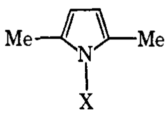
I



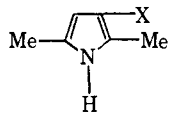
II



III



IV



V

reactor. Compounds I–III were thermolyzed at temperatures ranging from 466 to 550°, and IVa and IVb were thermolyzed at temperatures ranging from 387.5 to 450.6° and from 436.5 to 483.0°, respectively.

---

[1] On leave of absence from the Laboratory of Instrumental Analysis, University of Technology, Eindhoven, The Netherlands.

[2] I. A. Jacobson, Jr., H. H. Heady, and G. V. Dinneen, *J. Phys. Chem.*, **62**, 1563 (1958); I. A. Jacobson, Jr., and H. B. Jensen, *ibid.*, **66**, 1245 (1962); **68**, 3068 (1964).

[3] L. A. Pine, *Diss. Abstr.*, **24**, 522 (1963).

[4] J. M. Patterson and S. Soedigdo, *J. Org. Chem.*, **33**, 2057 (1968).

[5] (a) J. M. Patterson and L. T. Burka, *J. Amer. Chem. Soc.*, **88**, 3671 (1966); (b) J. M. Patterson, L. T. Burka, and M. R. Boyd, *J. Org. Chem.*, **33**, 4033 (1968).

[6] (a) J. W. de Haan and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **87**, 298 (1968); (b) W. C. Herndon and J. M. Manion, *J. Org. Chem.*, **33**, 4504 (1968).

[7] A. Jefferson and F. Scheinmann, *Quart. Rev. Chem. Soc.*, **22**, 391 (1968).

[8] Y. Makisumi and T. Sasatani, *Tetrahedron Lett.*, 543 (1969); Y. Makisumi, *ibid.*, 6413 (1969).

[9] S. J. Rhoads in "Molecular Rearrangements," Vol. 1, P. de Mayo Ed., Interscience, New York, N. Y., 1964, p 655.