to be converted into organic nitro compounds, aldehyde and/or nitroso secondary amine.

**Degradation of *p*-Methoxyhydrocinnamyl-*x*-$^{14}$C Alcohol.**—The acetylation and pyrolysis of *p*-methoxyhydrocinnamyl-*x*-$^{14}$C alcohol was carried out as described in the preparation of inactive *p*-methoxyallylbenzene. From 6.4 g. (0.038 mole) of the active carbinol, there was obtained 2.0 g. (35%) of *p*-methoxyallylbenzene-*x*-$^{14}$C.

To a stirred solution of 1.5 g. (10 mmoles) of *p*-methoxyallylbenzene-*x*-$^{14}$C in 20 ml. of 98–100% formic acid was added 0.9 ml. of 30% hydrogen peroxide solution. The mixture was stirred for 10 minutes, an additional 0.9 ml. of 30% hydrogen peroxide solution was added and the reaction allowed to continue at room temperature for 40 minutes. The solvent was removed under reduced pressure, the residue was boiled under reflux for 30 minutes with aqueous methanolic sodium hydroxide and the product was recovered by continuous ether extraction. The crude 3-(*p*-methoxyphenyl)-propane-1,2-diol-*x*-$^{14}$C was stirred for 2 hours at room temperatures with 1.5 g. of anhydrous potassium carbonate and 4.4 g. (10 mmoles) of lead tetraacetate in about 10 ml. of benzene. Formaldehyde-$^{14}$C was recovered from the reaction mixture by extraction with water and converted[21] into its dimethone derivative, m.p. 191.2–191.7° after recrystallization from methanol. The benzene was evaporated from the filtered solution of *p*-methoxyphenylacetaldehyde and the residue taken up in 80% ethanol, filtered and treated with excess methone.[21]

The dimethone derivative of *p*-methoxyphenylacetaldehyde was recrystallized from aqueous methanol, cyclohexane and finally from methanol, m.p. 152.5–154.5°.

*Anal.* Calcd. for $C_{25}H_{32}O_5$: C, 72.79; H, 7.82. Found: C, 73.00; H, 7.91.

A sample of *p*-methoxyhydrocinnamyl-*x*-$^{14}$C alcohol was oxidized with alkaline permanganate to anisic acid, m.p. 183.8–184.2° after recrystallization from benzene.

**Degradation of *p*-Methoxyallylbenzene-*x*-$^{14}$C.**—*p*-Methoxyallylbenzene-*x*-$^{14}$C (1.7 g., 11 mmoles) was hydroxylated and cleaved as described in the degradation of *p*-methoxyhydrocinnamyl-*x*-$^{14}$C alcohol. The yield of the dimethone derivative of formaldehyde-$^{14}$C, m.p. 191.3–191.7°, was 1.6 g. (50% over-all). The yield of the dimethone derivative of *p*-methoxyphenylacetaldehyde-$^{14}$C, m.p. 153.5–155.5°, was 1.3 g. (28% over-all).

**Degradation of *p*-Methoxybenzylmethylcarbinol-*x*-$^{14}$C.**—*p*-Methoxybenzylmethylcarbinol-*x*-$^{14}$C (6.3 g., 0.038 mole) was oxidized with 3.9 g. (0.039 mole) of chromium trioxide in aqueous acetic acid at room temperature. The crude product of the oxidation was diluted with inactive anisylacetone (6.3 g.). Distillation under reduced pressure gave a forerun (1.2 g.) which was discarded and 7.1 g. of anisylacetone-*x*-$^{14}$C, b.p. 114–117° (4.3 mm.). The 2,4-dinitrophenylhydrazone was prepared for $^{14}$C-activity measurements and had m.p. 107.7–108.1° after several recrystallizations from ethanol.

*Anal.* Calcd. for $C_{16}H_{16}N_4O_5$: C, 55.81; H, 4.68; N, 16.27. Found: C, 55.69; H, 4.74; N, 16.20.

Anisylacetone-*x*-$^{14}$C (6.8 g., 0.039 mole) was heated with 2.2 g. (0.020 mole) of *o*-phenylenediamine under an atmosphere of nitrogen for several hours at 250°. Several recrystallizations of the crude product from aqueous methanol followed by two sublimations gave about 0.5 g. of 2-(*p*-methoxybenzyl)-benzimidazole, m.p. 165.5–166°.

*Anal.* Calcd. for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.66. Found: C, 75.62; H, 5.94; N, 11.76.

The picrate of 2-(*p*-methoxybenzyl)-benzimidazole was prepared in ethanol solution and recrystallized from ethanol, m.p. 188–189°.

*Anal.* Calcd. for $C_{21}H_{17}N_5O_8$: N, 15.52. Found: N, 15.52.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

# An Oxygen-18 Tracer Study of the Rearrangement of *p*-Methoxy-*p*′-nitrobenzoyl Peroxide

BY DONALD B. DENNEY[1]

RECEIVED SEPTEMBER 16, 1955

*p*-Methoxy-*p*′-nitrobenzoyl peroxide (III) labeled with oxygen-18 in the anisoyl carbonyl has been rearranged to *p*-methoxyphenyl-*p*-nitrobenzoyl carbonate (IV). Upon hydrolysis IV afforded *p*-methoxyphenol containing no excess oxygen-18. These results exclude the formation of a positive anisate fragment VI as an intermediate in the rearrangement, but are in agreement with a mechanism which involves a concerted shift of *p*-methoxyphenyl to oxygen as the O–O bond undergoes heterolysis.

Within the last few years, it has been shown by many workers that certain compounds containing the peroxidic linkage can decompose or rearrange by heterolysis as well as homolysis of the O–O bond.[2]

Considerable interest has been expressed concerning the nature of the oxygen cation which could be an intermediate in these reactions. It has been recognized[2a] that if the oxygen cation does exist, it is probably a very short lived entity. Recent work from this and other laboratories[3–5] has shown that the rearrangement of 9-decalyl perbenzoate proceeds in such a manner that the formation of a free oxygen cation as an intermediate is very unlikely; the reaction is however definitely ionic in character. Bassey[6] and co-workers have studied the acid-catalyzed decomposition of 1-phenylethyl hydroperoxide in $H_2O^{18}$. They found that recovered hydroperoxide did not contain excess oxygen-18. They conclude that the reaction probably does not involve the formation of the oxygen cation as an intermediate, as it would presumably react with water to reform hydroperoxide which in their experiment should contain excess oxygen-18.

Leffler[7] has shown that *p*-methoxy-*p*′-nitrobenzoyl peroxide (III) can decompose in a homolytic or heterolytic manner, the mode of decomposition being governed to a large degree by the polarity of the solvent. When thionyl chloride is used as the solvent, the main product of the reaction is the mixed carbonate IV. It has been postulated that this reaction proceeds by heterolysis of the O–O bond to give the cation VI and *p*-nitrobenzoate ion.

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[1] School of Chemistry, Rutgers University, New Brunswick, N. J.

[2] For several examples of these reactions and pertinent discussions see (a) P. D. Bartlett, *Rec. Chem. Progr.*, **11**, 47 (1950); (b) J. E. Leffler, *Chem. Revs.*, **45**, 385 (1949); (c) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 107–122.

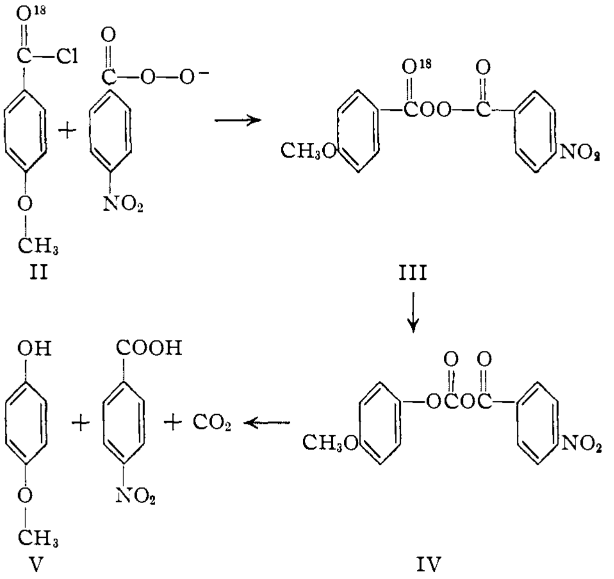
[3] D. B. Denney, THIS JOURNAL, **77**, 1706 (1955).

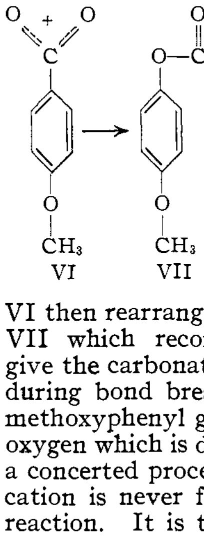
[4] P. D. Bartlett and J. L. Kice, *ibid.*, **75**, 5591 (1953).

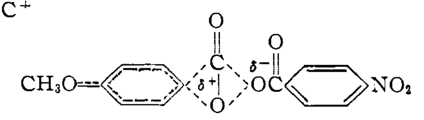
[5] H. L. Goering and A. C. Olson, *ibid.*, **75**, 5853 (1953).

[6] M. Bassey, C. A. Bunton, A. G. Davies, T. A. Lewis and D. R. Llewellyn, *J. Chem. Soc.*, 2471 (1955).

[7] J. E. Leffler, THIS JOURNAL, **72**, 67 (1950).




VI VII


VIII

VI then rearranges to the anisyloxycarbonyl cation VII which recombines with $p$-nitrobenzoate to give the carbonate IV. Another possibility is that during bond breaking of the O–O linkage the $p$-methoxyphenyl group migrates specifically to that oxygen which is developing the positive charge, *i.e.*, a concerted process is taking place and the oxygen cation is never formed as an intermediate in the reaction. It is the purpose of the work reported here to distinguish between these two possibilities.

Anisoyl chloride (II) labeled with oxygen-18 in the carbonyl group was prepared from anisic acid–$CO^{18}O^{18}H$ with thionyl chloride. The labeled acid was obtained by hydrolyzing anisoyl chloride in $H_2O^{18}$. II was converted to the labeled peroxide III which was rearranged in thionyl chloride to the labeled carbonate IV. In a trial run IV was obtained exactly as described by Leffler; however, in the tracer run, in which specially purified thionyl chloride was used as solvent, the product was contaminated with what appears to be anhydride. This is evidenced by a splitting of the 5.51 $\mu$ band of authentic carbonate into a band at 5.51 $\mu$ with a shoulder at 5.56 $\mu$ in the labeled material. In other respects the spectra are practically identical. The contaminant could not be removed by crystallization, but it did not interfere with the hydrolysis and $p$-methoxyphenol was isolated in good yield. Since the peroxide was not analyzed for oxygen-18, (because of its tendency to foul the train) it was important to establish that the carbonate IV contained excess oxygen-18 as it is theoretically possible that the carbonyl could have exchanged during the preparation of the peroxide. This was not the case as the analytical values show. Basic hydrolysis of IV provided $p$-methoxyphenol which contained no excess oxygen-18. Since it has been shown that phenol[8] and sodium phenolate[9] do not exchange their oxygens with water, the only conclusion that can be drawn from these results is that excess oxygen-18 never entered into the $p$-methoxyphenol. Since both oxygens of the cation VI are equivalent, if it had existed one would expect 50% of the excess oxygen-18 to be in the $p$-methoxyphenol. Clearly VI was not formed. An explanation which is consistent with these findings and with the other work cited is that a concerted shift of the $p$-methoxyphenyl occurred as the O–O bond broke. Since the cation VI has several possibilities for resonance stabilization, one would expect it to be one of the more stable oxygen cations, if such can exist. Since it was not formed, it seems worthwhile to amplify earlier suggestions by saying that the likelihood of obtaining a free oxygen cation under usual experimental conditions is very slight indeed.

In the rearrangement of 9-decalyl perbenzoate, the role of the anion has been shown to be very specific, *i.e.*, the benzoate ion is never free and migrates from oxygen to carbon with complete retention of its structural integrity. The rearrangement of III could proceed by a similar path; VIII would then represent the transition state or intermediate in the reaction. Some information could be obtained concerning the role of the anion by conducting the rearrangement in the presence of foreign anion. We have found, however, that IV is itself quite unstable to lithium $p$-chlorobenzoate in dimethylformamide, therefore exchange experiments would be of dubious value. In principle, labeling the carbonyl of the $p$-nitrobenzoyl group should throw considerable light on the role of the cation in this rearrangement and such experiments are planned for the near future.

## Experimental[10]

**Anisic Acid-$CO^{18}O^{18}H$** (I).—Anisoyl chloride, 25.0 g. (0.147 mole), was added dropwise with stirring over one hour to 50 ml. of water containing 1.57 atom % oxygen-18. The mixture was stirred and heated for 24 hours, cooled and filtered. The dried acid was crystallized from benzene to give 21.6 g. (97%) of I, m.p. 182.6–184°. The anisic acid contained 0.86, 0.86 atom % oxygen-18 calculated for localization in the carboxyl group. If complete exchange had taken place each oxygen of the carboxyl should have had *ca.* 1.55 atom % oxygen-18, rather than 0.86 as was found. These results indicate that the bulk of the oxygen-18 was introduced by hydrolysis of the chloride and very little by further exchange with the carboxyl. That this is the case is indicated by an earlier experiment in which anisic acid was refluxed with an acidic $H_2O^{18}$–tetrahydrofuran solution for 12 hours. Analysis of the recovered acid showed 0.26 atom % oxygen-18 in the carboxyl group or only 0.06 atom % enrichment. We attribute the very slow rate of exchange of anisic acid to (1) low solubility and (2) decreased reactivity of the carboxyl group because of the $p$-methoxyl substituent.

**Anisoyl Chloride-$CO^{18}Cl$** (II).—The labeled I, 21.0 g. (0.138 mole), was refluxed for two hours with 50 ml. of

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[8] M. Cohn and H. C. Urey, THIS JOURNAL, **60**, 679 (1938).

[9] I. A. Makalkin, *Acta Physicochim. U.R.S.S.*, **16**, 88 (1942); *C. A.*, **37**, 2355 (1943).

[10] The oxygen-18 analyses were conducted using the method of W. E. Doering and E. Dorfman, THIS JOURNAL, **75**, 5595 (1953). Normal isotopic abundance was taken as 0.204% $O^{18}$. Melting points are corrected.

thionyl chloride. The excess thionyl chloride was removed *in vacuo* and the acid chloride was distilled b.p. 142–144° (17 mm.) to give 19.3 g. (82%).

The anilide was prepared and after crystallization from methanol had m.p. 172–173°. Oxygen analysis 0.87, 0.87 atom % oxygen-18 calculated for localization in the carbonyl.

**$p$-Methoxy-$p'$-nitrobenzoyl Peroxide–Anisoyl Carbonyl-$O^{18}$ (III).**—This compound was prepared according to Leffler's procedure. From 17.8 g. (0.105 mole) of anisoyl chloride–$CO^{18}Cl$ there was obtained after crystallization from acetone–pentane 3.4 g. (11%) of III, m.p. 108–108.5°.

**Labeled $p$-Nitrobenzoyl-$p$-methoxyphenyl Carbonate (IV).**—The mixed peroxide III, 3.2 g. (0.010 mole), was heated for 1.5 hours under reflux in 50 ml. of purified thionyl chloride.[11] The thionyl chloride was removed *in vacuo* to give a solid which was crystallized from acetone–hexane twice to give 0.70 g. of material which softened at 106° and formed a very viscous melt at 122°. A sample of IV prepared in a trial run softened at 121° and melted 126–128°, after standing for five months this sample melted from 121–127°. A pinkish color had developed in the sample indicating the presence of $p$-methoxyphenol. The infrared spectra of labeled IV and unlabeled IV were identical except for a shoulder at 5.56 μ in the labeled sample which did not appear in the unlabeled material. We attribute this to $p$-nitrobenzoic anhydride which could be easily formed under the conditions of the reaction. A mixed melting point of labeled IV and unlabeled IV was 120–127°. Oxygen-18 analysis showed 0.65, 0.68 atom % oxygen-18 calculated for localization in one position. On the basis of the acid and anilide the analysis should have been 0.86 atom % oxygen-18.

**$p$-Methoxyphenol (V).**—The carbonate IV, 0.50 g. (0.00158 mole), was refluxed for 15 min. with 0.50 g. (0.0125 mole) of sodium hydroxide in 8 ml. of water. The mixture was cooled, acidified to $p$H 7 and extracted with three 10-ml. portions of ether. The ether was washed with 5 ml. of water and then dried over magnesium sulfate. The ether was evaporated to give 0.16 g. of an oil which crystallized from water to afford 0.09 g. (53%) of $p$-methoxyphenol, m.p. 54–55°, infrared identical with that of an authentic sample of $p$-methoxyphenol. Oxygen-18 analysis 0.19, 0.19 atom % oxygen-18. An authentic sample showed 0.20 atom % oxygen-18.

NEW HAVEN, CONN.

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[11] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, pp. 381.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

# Neighboring Carbon and Hydrogen. XXI.[1] *Anti*-7 Derivatives of Norbornene[2] (Bicyclo[2.2.1]heptene) as Homoallylic Systems[3a]

BY S. WINSTEIN AND M. SHATAVSKY[3b]

RECEIVED JULY 7, 1955

The mixture of dibromides obtained from bromine addition to bicycloheptadiene contains an unsaturated component which is very reactive in solvolysis. The solid glycol derived from treatment of the dibromide with aqueous permanganate is no longer unusually reactive in solvolysis. Debromination of the dibromoglycol with zinc–copper couple yields initially a very unreactive monobromoglycol. Further debromination yields *exo-cis*-2,3-dihydroxynorbornane. On the basis of this evidence and the dipole moment of the acetonide of the dibromoglycol the unsaturated dibromide is taken to be *exo*-5-*anti*-7-dibromonorbornene. Selective hydrolysis of the more reactive halogen atom of the unsaturated dibromide gives rise to *exo*-5-bromo-*anti*-7-hydroxynorbornene. This bromohydrin yields a toluenesulfonate which is very reactive in acetolysis. Zinc debromination of the bromohydrin and hydrogenation of the *anti*-7-hydroxynorbornene gave rise to 7-hydroxynorbornane, identical with a specimen supplied by R. B. Woodward and C. Norton. The toluenesulfonate of the 7-hydroxynorbornene is twenty-five times as reactive as the *exo*-5-norbornenyl ester and $2 \times 10^5$ times as reactive as the *endo*-5-norbornenyl derivative. The *anti*-7-norbornenyl system should be classed as a homoallylic one along with others like cholesteryl and 5-norbornenyl. However, it is geometrically quite unique. The full extent of anchimeric assistance to ionization of *anti*-7-norbornenyl $p$-toluenesulfonate may be appreciated from the factor of *ca.* $10^{11}$ between acetolysis rates of *anti*-7-norbornenyl $p$-toluenesulfonate and its saturated analog which has been studied by Woodward and Norton.

As shown elsewhere,[4] the dibromide from addition of bromine to bicycloheptadiene I contains an unsaturated component which has been concentrated somewhat but not isolated separately. This unsaturated dibromide is unusually reactive in solvolysis by comparison with the saturated dibromonortricyclenes also obtained. Similarly,[4] the bromoether obtained on treatment of bicycloheptadiene I with N-bromosuccinimide in methanol also contains a highly reactive unsaturated component. In Table I are given the relative reactivities of the unsaturated dibromide and the unsaturated bromoether relative to *exo*-5-bromonorbornene[4] in 80% alcohol. The dibromide is twenty-three times as reactive, and the bromoether 190 times as reactive, as the *exo*-5-bromonorbornene even before correction for the rate-retarding polar effect of the second halogen atom[5] or the methoxyl group[5] on solvolysis rate.

TABLE I

COMPARISON OF REACTIVITY OF SOME DEHYDRONORBORNYL BROMIDES IN 80% EtOH

| Compound | Temp., °C. | $k$, hr.$^{-1}$ | Rel. rate[a] 25° |
|---|---|---|---|
| XIV | 75.0 | 1.0 | 1 |
| XV | 75.0 | 1.90 ± 0.02 | 2 |
| II | 24.8 | 0.043 | 23 |
| | 50.0 | 1.0 | |
| *exo*-5-Methoxy-*anti*-7-norbornene[4] | 25.1 | 0.36 | 190 |

[a] Approximated on the basis of identical $\Delta S^{\pm}$ for the first three compounds.

Considerations of mechanism of halogen addition[4] with or without carbon participation suggested II, III and IV as possible structures of the reactive

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[1] Paper XX: S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, THIS JOURNAL, **77**, 4183 (1955).

[2] See A. M. Patterson, *Chem. Eng. News*, **30**, 930 (1952), for nomenclature.

[3] (a) Research supported by grants from Julius Hyman and Co., Denver, Colo., and later the Julius Hyman Division of Shell Chemical Co.; (b) deceased, summer, 1954.

[4] S. Winstein and M. Shatavsky, *Chemistry and Industry*, in press.

[5] *E.g.*, S. Winstein, *et al.*, THIS JOURNAL, **70**, 816, 821, 828 (1948); E. Grunwald, *ibid.*, **73**, 5458 (1951).