Ozonolysis of Naphthalenes. The Aliphatic Products and Mechanism

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Further evidence for the course of ozonolysis in methanol of naphthalene and certain substituted naphthalenes has been obtained by v.p.c. examination of the decomposition products of the hydroperoxides formed from carbons 2 and 3 of the naphthalene ring system. These products are compared with the decomposition products of certain olefinic compounds which should give the same hydroperoxides upon ozonolysis in methanol. In two cases the products from ozonolysis of only one bond of the naphthalene nucleus have been studied. Evidence is presented for the stage at which ozonolysis of 2-alkoxynaphthalenes differs from that of β-naphthol and the other naphthalenes studied.

The preceding paper[1] discusses the aromatic peroxidic and nonperoxidic ozonolysis products of naphthalene (Ia), 2,3-dimethylnaphthalene (Ib), 2-naphthol (Ic), 2-methoxy- (Id), and 2-ethoxynaphthalene (Ie). From ozonolyses of Ia, Ib, and Ic in methanol the major peroxidic product was 4-methoxy-2,3-benzodioxan-1-ol (IV), whereas from Id and Ie under the same conditions it was 1,4-dimethoxy-2,3-benzodioxan (Xb). Evidence was presented that IV arose from cyclization of II, produced along with peroxides III which were not isolated, and that the precursor to Xb was IX, produced along with methyl or ethyl glyoxalate (VIIId or e) which were isolated.

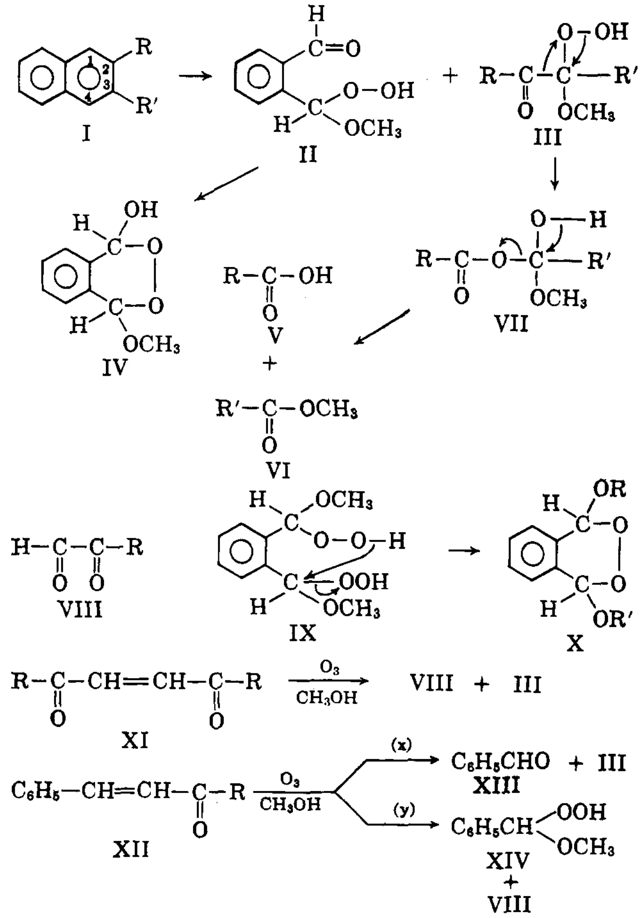
Since the yields of IV from Ib and Ic were not high, and since the possibility was not entirely eliminated that Xb could have arisen from IV, and VIIId or e from the corresponding peroxides III (*e.g.* VIIId from IIId or IIIj), it was important to check the validity of the proposed reaction courses by seeking evidence for or against peroxides III in the ozonolysis reaction mixtures.

Thus, the present paper reports a study of the aliphatic ozonolysis products (involving carbons 2 and 3) of Ia, Ib, Ic, Id, Ie, 2-methylnaphthalene (If), 1-methylnaphthalene, and 1,4-dimethylnaphthalene. The latter three compounds were included because, although some of the nonperoxidic ozonolysis products are known, the route to these substances was not fully elucidated,[2,3] and it was of interest to compare the reaction courses in methanol of these three with those of the other naphthalene compounds studied. The paper also discusses partial ozonolysis products (from cleavage of the 1,2 bond of Ic and Id) and the mechanism of ozonolysis of the naphthalene ring system.

Peroxides III proved to be too unstable to isolate, although their presence was indicated by iodide reduction of the dilute ozonolysis mixtures of Ia and Ib, which showed 1 mole equiv. of active oxygen; peroxide IV under these conditions undergoes rearrangement rather than reduction.[1]

Compounds III were studied by means of quantitative v.p.c. determinations of the volatile aliphatic ozonolysis decomposition products of the various naphthalene compounds. The results, shown in Table I, were compared with the results of similar studies with several olefinic compounds which should give identical peroxides III upon ozonolysis, and with the results of Bailey and Chang[4] with several α-alkoxy-α-hydroperoxyacophenones (*e.g.* IIIh). These peroxides decompose in methanol to an acid and an ester, presumably *via* a concerted rearrangement (*e.g.* IIIh → VIIh → Vh + VIh).

Scheme I



a, R = R′ = H
b, R = R′ = CH_3
c, R = OH; R′ = H
d, R = OCH_3; R′ = H
e, R = OEt; R′ = H
f, R = CH_3; R′ = H
g, R = H; R′ = CH_3
h, R = phenyl; R′ = H
i, R = R′ = Et
j, R = H; R′ = OCH_3
k, R = CH_3; R′ = Et

The compounds studied for comparison with the naphthalenes were fumaric acid (XIc), methyl fumarate (XId), and ethyl fumarate (XIe), which should give the corresponding III and VIII compounds, and *trans*-cinnamaldehyde (XIIa), which should give at least some IIIa. It had been desired to study maleic dialdehyde (XIa) which should give only IIIa and VIIIa, whereas XIIa, according to the Criegee mechanism,[5,6]

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[1] P. S. Bailey, S. S. Bath, F. Dobinson, F. J. Garcia-Sharp, and C. D. Johnson, *J. Org. Chem.*, **29**, 697 (1964).

[2] R. H. Callighan and M. H. Wilt, *ibid.*, **26**, 5212 (1961).

[3] L. W. F. Kampschmidt and J. P. Wibaut, *Rec. trav. chim.*, **73**, 431 (1954).

[4] P. S. Bailey and Y. G. Chang, *J. Org. Chem.*, **27**, 1192 (1962).

[5] P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

[6] P. S. Bailey, S. B. Mainthia, and C. J. Abshire, *J. Am. Chem. Soc.*, **82**, 6136 (1960).

TABLE I

VAPOR PHASE CHROMATOGRAPHY DETERMINATIONS OF VOLATILE PRODUCTS FROM OZONOLYSES OF NAPHTHALENES

Compound	CO_2	$HCOOCH_3$[a]	CH_3COOCH_3[a]	HCOOH[a]	CH_3COOH[a]	Total yield, %[a]
Naphthalene (Ia)	Small peak	1.3	0	0.3	0	80
2,3-Dimethylnaphthalene (Ib)	Small peak	<0.1	1.25	0.1	0.35	85[b]
1,4-Dimethylnaphthalene	Small peak	1.3	<0.1	0.5	0	90
1-Methylnaphthalene	Small peak	1.3	0.3	0.1	0	85
2-Methylnaphthalene (If)	Small peak	1.1	0.8	0.1	<0.1	100
2-Naphthol (Ic)	Large peak	0.8	0	<0.1	0	80
2-Methoxynaphthalene (Id)	Small peak	<0.1	0	0	0	<5[c]

[a] Moles per mole of naphthalene compound. Total yield based on products expected from the corresponding III. [b] No trace of biacetyl could be detected. [c] From ozonolysis in ethanol, identical results were obtained, except that the product was ethyl formate.

TABLE II

VAPOR PHASE CHROMATOGRAPHY DETERMINATIONS OF OZONOLYSIS PRODUCTS OF COMPOUNDS XI AND XII[a]

Compound	VIII[b,c]	CO_2	$HCOOCH_3$[c]	HCOOH[c]	Oxalate[b,c]	XIII[c]	$C_6H_5COOCH_3$[c]
XIc		Large peak	0.8	0			
XId	1.0	Large peak	0.4	0	0.6		
XIe[d]	1.0	Large peak	0.4	0	0.6		
trans-stilbene						1.2	0.8
XIIa		Small peak	0.6	0.3	0	0.60	0.35
XIIc (*cis*)		Large peak	0.5[e]			0.60	0.25
XIIc (*trans*)		Large peak	0.5[e]			0.65	0.30
XIId (*cis*)	0.95	Small peak	0.05	0	0.05	0.15	0.70
XIId (*trans*)	0.95	Small peak	0.05	0	0.05	0.15	0.70

[a] The ozonolysis solvent was methanol. For a description of the techniques used, see Experimental section. Column 1 was used for the v.p.c. determinations. [b] Compounds VIII and the oxalate (XXI) compound corresponded in group R to the compound ozonized; *e.g.*, XId gave VIIId and XXIb. [c] Yields are in moles per mole of compound ozonized. [d] Ethanol also was detected by v.p.c. [e] Obtained only after refluxing the reaction mixture for 30 min.

could yield either IIIa and XIII (route x) or XIV and VIIIa (route y). However, we were not able to obtain the compound in a pure enough state[7] to give reliable results.

The v.p.c. data from the ozonolysis mixtures of these compounds are shown in Table II. Included also are *cis*- and *trans*-cinnamic acids (XIIc), the *cis*- and *trans*-methyl cinnamates (XIId), and *trans*-stilbene, which were ozonized for reasons to be described later.

Table I shows that formic acid (Va) and methyl formate (VIa) were obtained in 80% yield from ozonolysis of naphthalene (Ia) in methanol. The same products were obtained in 45% yield from *trans*-cinnamaldehyde (XIIa, Table II). Both this result and the yields of XIII and methyl benzoate, in comparison with those from *trans*-stilbene, indicate an approximate 50% yield of IIIa from XIIa. The excess methyl formate over formic acid obtained from both naphthalene and XIIa could be due either to esterification in the presence of the large excess of methanol, or to minor fates of III observed in the decomposition studies with the α-hydroperoxy-α-methoxyacophenones (*e.g.*, IIIh).[4]

Similarly, 2,3-dimethylnaphthalene (Ib) gave the products expected from IIIb, and 1,4-dimethylnaphthalene and 1-methylnaphthalene gave the products expected from IIIa, predominantly (Table I). The small amounts of formic acid and methyl formate obtained from Ib and of methyl acetate from 1-methylnaphthalene and 1,4-dimethylnaphthalene indicate either minor competing ozonolyses of the nonmethylated ring, as proposed also by other workers,[3] or minor rearrangements of II or IV and methyl analogs thereof. Since both acetic and formic acids were obtained from 2-methylnaphthalene (If, Table I), it is likely that both IIIf and IIIg were produced, along with IV. It is not possible to be more exact than this, however, since extensive esterification obviously occurred, and some of the formic acid and methyl formate obtained could have come from the competing ozonolysis of the nonmethylated ring.

Since the results with all five of these naphthalene compounds fit well the expected results from the respective peroxides III by analogy to the similar α-hydroperoxy-α-methoxyacophenones (*e.g.*, IIIh),[4] and since both naphthalene (Ia) and *trans*-cinnamaldehyde (XIIa) gave the volatile products expected from IIIa, it was not considered necessary to compare the 2-methyl- and 2,3-dimethylnaphthalene results with those of olefinic compounds which should yield IIIb, IIIf, or IIIg upon ozonolysis.

Thus, v.p.c. determinations of the volatile ozonolysis products of naphthalene and the methylated naphthalenes verify the proposal[1] that the initial ozonolysis products are II (or its methyl analogs) and III.

Ozonolysis of fumaric acid (XIc) in methanol (Table II) gave carbon dioxide and methyl formate, products expected from IIIc by analogy to IIIh (*i.e.*, XVa → XVIa → XVIIa + XVIII). Some carbon dioxide was evolved during the ozonolysis; the rest was obtained on the v.p.c. column. Ozonolysis of dimethyl fumarate (XId) in methanol (Table II), however, gave not only methyl glyoxalate (VIIId), carbon dioxide, and methyl formate, but also dimethyl oxalate (XXIb). Similarly, carbon dioxide, methyl formate, VIIIe, and XXIc were obtained from ozonolysis of diethyl fumarate (XIe) in methanol (Table II). The same analyses were obtained whether the hydroperoxides were decomposed on the column or by refluxing the methanolic reaction mixtures. Thus, there appear to be two competing ionic decomposition routes for peroxides IIId and IIIe, one analogous to that for IIIh[4] (XV → XVI → XVII

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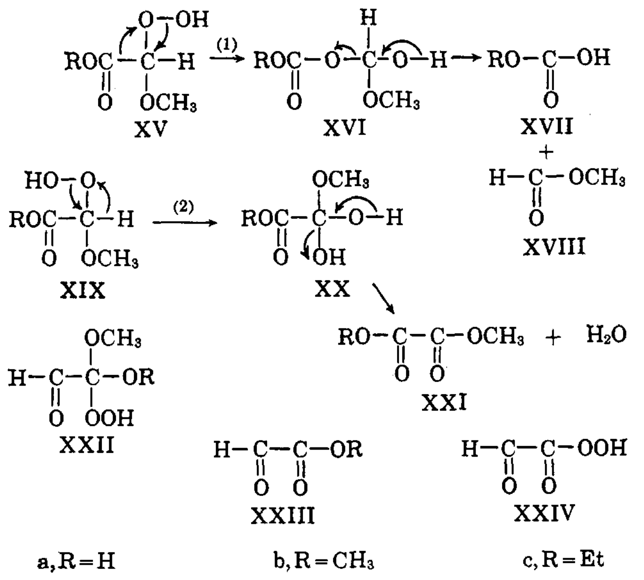
(7) Method of D. L. Hufford, D. S. Tarbell, and T. R. Koszalka, *J. Am. Chem. Soc.*, **74**, 3014 (1952).

SCHEME II



+ XVIII), occurring to the extent of 40%, the other (XIX → XX → XXI) to the extent of 60%[8] (Scheme II). Perhaps the same competition exists with IIIc, since the carbon dioxide evolved during the ozonolysis could have come from XVIIa, whereas that appearing on the column could have arisen from decarboxylation of XXIa to carbon dioxide and methyl formate (XVIII).

From ozonolysis of 2-naphthol (Ic) in methanol, either XVa (same as IIIc) or XXIIa could be produced along with II. The v.p.c. results (Table I) show the same products as obtained from fumaric acid (XIc, Table II), indicating that XVa is formed predominantly. In contrast, XXIIa might be expected to undergo one of the following reactions: (1) eliminate methanol and produce perglyoxalic acid (XXIV), (2) eliminate hydrogen peroxide to yield methyl glyoxalate (XXIIIb), or (3) rearrange in the general manner of peroxides III[4] to give formic acid and carbon dioxide. Since formic acid could be esterified in the methanolic solution, however, XXIIa remained a possibility. Further evidence that β-naphthol gives XVa, predominantly, was obtained as follows.

Bernatek and Frengen[9] have obtained *o*-carboxycinnamic acid (XXVIIb) from ozonolysis of 2-naphthol (Ic) in nonparticipating solvents, showing that ozone attacks the bonds of 2-naphthol stepwise rather than simultaneously (*i.e.*, through XXVb rather than XXIXb). This same compound was obtained in 53% yield by treatment of Ic in methanol with 1 mole equiv. of ozone, and decomposing the cold reaction mixture in cold water. This indicates that XXVIb rather than XXXb is predominantly produced initially, and reacts further with ozone through XXVIIIb to give II and IIIc (same as XVa). Although the point is not proven, since it is possible for XXVIIb to be produced through either intramolecular or intermolecular interaction of the hydroperoxy and aldehyde groups of XXXb, the mild conditions and short reaction time speak against the latter possibility, and the cumulative evidence already given and yet to be presented (ozonolyses of XIIc and XIId) heavily support the reaction course proposed.

The low isolated yield of IV from 2-naphthol (Ic) in comparison to that from naphthalene (Ia) is perhaps partially due to some decomposition at stage XXVIb. In addition, however, it has been observed that 0.1 to 0.2 mole equiv. of molecular oxygen is evolved during ozonation of 2-naphthol in methanol with an ozone–nitrogen mixture, indicating some atom attack products.[10] Further, a deep orange color develops during the early stages of the ozonation.[1] It is suggested, therefore, that reactions such as indicated by Ic → XXXI → XXXII occur to the extent of 5–10%. In contrast, no such color develops during the ozonation of naphthalene, and the oxygen yield indicates only 3–5% atom attack.[11]

Ozonolysis of 2-methoxynaphthalene (Id) in methanol gave by v.p.c. a 95% yield of methyl glyoxalate (XXIIIb) and only traces of carbon dioxide and methyl formate; no dimethyl oxalate (XXIb) was obtained. Had the ozonolysis course with Id been similar to that with 2-naphthol (Ic), the aliphatic moiety would have been either IIId (same as XVb) or, perhaps, XXIIb. The fact that the known decomposition products of IIId (Table II) were not obtained, except perhaps in traces, prove that it is not produced to any appreciable extent from Id. Peroxide XXIIb has not been studied, however, and it is conceivable that Id could have reacted with ozone in methanol to give IV and XXIIb, after which XXIIb could have methylated IV to give Xb and XXIIa; the latter could then lose hydrogen peroxide to yield methyl glyoxalate (XXIIIb). This was shown not to be the case, however, by the fact that ozonolysis of 2-methoxynaphthalene (Id) in ethanol gave 1,4-diethoxy-2,3-benzodioxan (Xi) and methyl glyoxalate (XXIIIb), and ozonolysis of 2-ethoxynaphthalene (Ie) in methanol gave 1,4-dimethoxy-2,3-benzodioxan (Xb) and ethyl glyoxalate (XXIIIc).[1] If the mechanism stated above were correct, peroxide XXIIc should have been the initial aliphatic product in both cases just mentioned, and it should have produced either XXIIIb or XXIIIc or the same mixtures of the two in both instances described. In addition, Xk would have been expected from one or both reactions.

Thus, the mechanism proposed in the preceding paper[1] seems established for the ozonolysis of Id (or Ie) in methanol or ethanol solution (*e.g.*, Id $\xrightarrow[CH_3OH]{O_3}$ VIIId + IX → Xb). This means that the first product in the ozonolysis, similar to that proposed for Ic, must be XXVIc. The difference in results of ozonolysis of Ic and Id apparently comes then in further ozonolysis of XXVI, which gives II and IIIc in the case of XXVIb, but gives IX and VIIId in the case of XXVIc. Ozonolysis results with *cis*- and *trans*-cinnamic acid (XIIc) and *cis*- and *trans*-methyl cinnamate (XIId) support this proposal. It can be seen from Table II that XIIc gives largely benzaldehyde and IIIc, whereas XIId gives largely XIV and VIIIb. As will be discussed in

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[8] Dimethyl oxalate could have arisen also by decomposition of an adduct of XVb and methyl glyoxalate (XXIIIb). Such reactions will be discussed in a later paper.

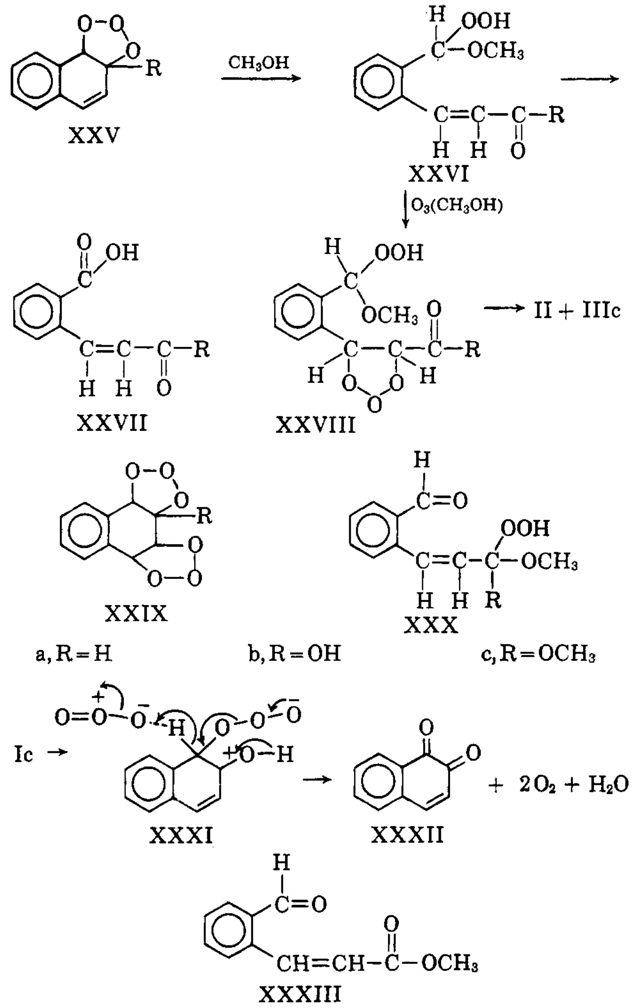
[9] E. Bernatek and C. Frengen, *Acta Chem. Scand.*, **16**, 2421 (1962).

[10] P. S. Bailey and A. M. Reader, *Chem. Ind.* (London), 1063 (1961).

[11] The atom attack of ozone is discussed in papers on ozonation of anthracene [F. Dobinson and P. S. Bailey, *ibid.*, 632 (1961)] and additional results to be published soon.[12]

[12] P. S. Bailey, P. Kolsaker, B. Sinha, J. B. Ashton, F. Dobinson, and J. E. Batterbee, *J. Org. Chem.*, **29**, in press.

SCHEME III



a later paper on reactions of these and similar peroxides, there is evidence that IIId will interact with benzaldehyde and oxidize it in methanol solution. However, the yields of the other products from such an interaction are very different from those obtained from ozonolysis of XIId (Table II).

It was hoped to obtain further evidence for the reaction course just outlined for Id by ozonolysis of only one bond, as was done with Ic. No definite product could be obtained, however, except by heat decomposition of the acidified reaction mixture followed by treatment with 2,4-dinitrophenylhydrazine, which gave the dinitrophenylhydrazone (DNP) of methyl *o*-formylcinnamate (XXXIII). This aldehyde ester (XXXIII) apparently is the main decomposition product of XXVIc under acidic conditions, which appears to promote decomposition of certain alkoxy-hydroperoxides to aldehydes.[13]

Ozonolysis of naphthalene (Ia) in methanol with 1 mole equiv. of ozone resulted in a 42% recovery of unchanged Ia. Thus one can not determine whether the first product (from XXVa) is XXVIa or XXXa.

Experimental[14]

Ozonolysis solvents were pure and anhydrous. All starting materials, except those whose preparations are described below, were obtained from commercial sources and were purified, if necessary, by usual procedures. **Dimethyl (XId) and diethyl (XIe) fumarates** were prepared by treating commercial fumaric acid (XIc) with an approximately 3% solution of anhydrous hydrogen chloride in the corresponding anhydrous alcohol; the dimethyl ester melted at 102°[15]; the diethyl ester boiled at 215–220°, $n^{25}{}_{\mathrm{D}}$ 1.4400.[16] **Methyl phenylpropiolate** was similarly prepared from commercially obtained phenylpropiolic acid; the crude yield was 93%. Commercial ***trans*-cinnamaldehyde** (XIIa) was purified by washing an ether solution of it with dilute sodium bicarbonate solution, after which it was distilled under reduced pressure to give $n^{25}{}_{\mathrm{D}}$ 1.6199.

***cis*-Methyl cinnamate** (XIId) was synthesized by hydrogenation of crude methyl phenylpropiolate (9.5 g.) in methanol (50 ml.) using Lindlar catalyst (4 g.). The hydrogen uptake was rapid until one mole equiv. had reacted. The catalyst was then removed by filtration (Celite) and the filtrate was evaporated. The residual oil was dissolved in ether, and the ether solution was dried and distilled, giving 6.1 g. of XIId (64%), b.p. 92–93° (1.2 mm.), $n^{26}{}_{\mathrm{D}}$ 1.5488.[17]

***cis*-Cinnamic acid (XIIc)** was prepared by refluxing a solution of 6.5 g. of the methyl ester (XIId) in 50 ml. of 10% aqueous sodium hydroxide solution for 1 hr. The reaction mixture was cooled, acidified, and extracted with ether, and the ether extract was dried and evaporated, giving 5.3 g. (90% yield) of crude, oily XIIc. Crystallization and recrystallization from petroleum ether (b.p. 40–60°) gave long white prisms melting at 67°. The reported[18] melting point for allocinnamic acid is 68°. The infrared spectrum was identical with that of the ini ial oil (which must be a mixture of the polymorphs of *cis*-cinnamic acid XIIc[18]), and showed the characteristic *cis* peak at 14.5 μ. The same material was obtained by hydrogenation of the sodium salt of phenylpropiolic acid,[19] using Lindlar catalyst, but the hydrogen uptake was slower and the yield was much poorer than in the case of the methyl ester hydrogenation.

Ozonolyses.—All ozonolysis solutions, except that of *trans*-stilbene, contained 0.01 mole of compound in 50 ml. of methanol (or ethanol). The solutions were maintained at about −30° during the ozonolyses. All of the compounds ozonized were completely soluble in the solvent, and ozone uptake was quantitative, with the exception of dimethyl fumarate. In this case some starting material remained undissolved at the beginning of the ozonolysis, and some ozone passed into the potassium iodide trap. The *trans*-stilbene was ozonized in a 1:1 mixture of methanol and methylene chloride for solubility reasons. Two mole equivalents of ozone were absorbed by the naphthalenes, whereas only 1 mole equiv. reacted with the other compounds. Care was taken to stop the stilbene and cinnamate ozonolyses just short of 1 mole equiv. of ozone, to prevent oxidation of benzaldehyde. The excess ozone was swept out with nitrogen and the ozonolysis reaction mixtures were allowed to stand at room temperature for 1 hr. before being examined by gas chromatography.

Gas Chromatographic Measurements of Ozonolysis Reaction Mixtures.—An F and M Model 500 gas chromatograph was employed. The columns used were (1) 20% Carbowax 1500 on acid-washed Chromosorb P, length 10 ft; (2) Carbowax 400 on acid-washed Chromosorb P, length 7 ft.; (3) 5% dimer acid silicone oil 550 on Haloport F, length 10 ft.; (4) 5% Celanese ester No. 9 on Haloport F, length 10 ft. Ten milliliters of each ozonolysis solution was injected into the chromatograph. Column 1 was used for the carbon dioxide and formate and acetate determinations at 60° and for the benzaldehyde, glyoxalate, oxalate, and benzoate determinations at 150°. The determinations on ozonized solutions of *trans*-stilbene and the methyl cinnamates were repeated on column 4 at 150°. On this column, XIV appeared to give entirely methyl benzoate upon decomposition. Column 4 also served to demonstrate that no phenol was formed during thermal decomposition of XIV. Column 2 was sometimes used in place of column 1 for the formate and acetate

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[13] Results to be reported later.

[14] Melting points are corrected. The ozonation set-up and technique was described in earlier papers [*e.g.*, P. S. Bailey and S. S. Bath, *J. Am. Chem. Soc.*, **79**, 3120 (1957)].

[15] J. DeWolf and L. van de Straete, *Bull. soc. chim. Belges*, **44**, 289 (1935).

[16] C. Knops [*Ann.*, **248**, 190 (1888)] reports $n^{20}{}_{\mathrm{D}}$ 1.4410.

[17] G. B. Kistiakowsky and W. R. Smith [*J. Am. Chem. Soc.*, **57**, 269 (1935)] report $n^{20}{}_{\mathrm{D}}$ 1.5528.

[18] (a) C. Liebermann and H. Trucksäss, *Ber.*, **42**, 4659 (1909); (b) H. V. W. Robinson and T. C. James, *J. Chem. Soc.*, 1453 (1933).

[19] C. Paal and W. Hartmann, *Ber.*, **42**, 3930 (1909).

determinations with the naphthalene ozonolysis mixtures. Column 3 was used for the formic and acetic acid determinations at 95°. The peaks obtained were compared with those from standard solutions, and yields were estimated by determination of peak areas with an integrator, and by peak heights. The latter did not always appear to give accurate results, however. Where peaks were obtained on the shoulders of other peaks (*e.g.*, formic acid on the shoulder of methanol), estimation was made of peak areas by cutting out and weighing, or by means of a planimeter. Most of the results are shown in Tables I and II. In addition, the yield of methyl glyoxalate (XXIIIb) was 95% from an ozonized solution of 2-methoxynaphthalene (Id) in methanol, and 70% from a similar ethanolic reaction mixture; the yield of ethyl glyoxalate (XXIIc) from an ozonized solution of 2-ethoxynaphthalene (Ie) in methanol was 100%. The standard in each case was an ozonized solution of the corresponding fumarate.

Ozonolyses of Naphthalenes with 1 Mole Equiv. of Ozone. A. Naphthalene (Ia).—A solution of 2.6 g. of naphthalene in 50 ml. methanol and 75 ml. methylene chloride was ozonized at −20°. The absorption of 1 mole equivalent of ozone was quantitative. The reaction mixture was evaporated; the residue was dissolved in a little methanol and treated with water. The precipitated naphthalene weighed 1.1 g. (42%) and melted at 72–75° (mixture melting point with known sample, 73°).

B. 2-Naphthol (Ic).—A solution of 2.9 g. (0.02 mole) of Ic in 100 ml. of methanol was ozonized with 1 mole equiv. of ozone at −20°. V.p.c. of the reaction mixture showed only a trace of methyl formate. The reaction mixture was partially evaporated and poured into 500 ml. of water. Some darkening and effervescing occurred and a precipitate formed, giving a 53% yield of *o*-carboxycinnamic acid (XXVIIb), melting at 186–189°, when recrystallized from acetic acid, m.p. 196°. The compound gave a negative test for carbonyl with Brady's reagent and its melting point and infrared spectrum corresponded well with that reported by Bernatek and Frengen.[9] In another instance the cold reaction mixture was poured immediately into cold water. The yield of XXVIIb was 46%.

Anal. Calcd. for $C_{10}H_8O_4$: neut. equiv., 96. Found: neut. equiv., 101.

C. 2-Methoxynaphthalene (Id).—A solution of 0.01 mole of Id in 50 ml. of a 1:1 mixture of methanol–methylene chloride was ozonized with 1 mole equiv. of ozone. V.p.c. showed only a trace of methyl glyoxalate. When the solution was poured into water, no precipitate was obtained, and evaporation or treatment with sodium hydroxide gave only red tars. The original solution was acidified with 3 drops of concentrated hydrochloric acid and refluxed for 1 hr., after which it was treated with excess 2,4-dinitrophenylhydrazine in ethanol–sulfuric acid. The DNP weighed 2.16 g. (58% yield) and melted at 192–199°, when recrystallized from benzene, m.p. 205–206°. The infrared spectrum (methylene chloride) was similar to that of the DNP of methyl phthalaldehydate, as would be expected for the DNP of XXXIII.

Anal. Calcd. for $C_{17}H_{14}N_4O_6$: C, 55.13; H, 3.81; N, 15.13; OCH_3, 8.38; mol. wt., 370. Found: C, 55.46; H, 4.08; N, 14.20, 16.13; OCH3, 8.25; mol. wt., 360.

Ozonizations with Ozone–Nitrogen and Molecular Oxygen Yields.—The procedure was as described in an earlier paper.[10] The results are shown in table form. By analogy to results with anthracene, in which 3 moles of oxygen were evolved per mole of anthraquinone in methylene chloride, and 2 moles of oxygen per mole of anthraquinone in methanol,[12] it is seen that the amount of atom attack is only 3–5% with naphthalene and 5–10% with 2-naphthol.

TABLE III

OXYGEN YIELDS USING OZONE–NITROGEN

Compound	mmoles used	Solvent	mmoles of O_3 reacted	mmoles of O_2 evolved
Naphthalene	10	$CH_3OH-CH_2Cl_2$, 1:1	20	0.68
Naphthalene	10	CH_2Cl_2	20	1.44
2-Naphthol	10	$CH_3OH-CH_2Cl_2$, 1:1	20	1.43

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The Preparation of 1-Amino-1-fluoroalkylethylenes by the Addition of Active Methylene Compounds to Fluoroalkyl Cyanides

A. D. JOSEY

*Contribution No. 864 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington, Delaware*

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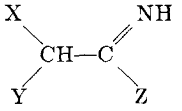
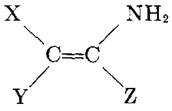
It has been shown that the addition of active methylene compounds to the cyano group of fluoroalkyl cyanides gives a new class of reactive intermediates, the 1-amino-1-fluoroalkylethylenes. Several reactions of these stable enamines have been studied including acylation of the acidic amino function and replacement of the latter by nucleophiles.

Addition of active methylene compounds to the cyano group have been explored to a considerable extent,[1] and while the products have often been formulated as substituted ketimines (I), it seems likely in view of more recent studies[2] that in many cases the enamine structure (II) is the preferred arrangement.



I



II

The addition of malononitrile, cyanoacetic ester, and malonic ester to the exceptionally reactive cyano group of fluoroalkyl cyanides gives stable crystalline products in yields ranging from 55–100%. The formulation of the products as primary enamines receives support from infrared spectra which disclose the $-NH_2$ group as well as the carbon–carbon double bond conjugated with the electronegative group of the active methylene compound. In addition, the ultraviolet spectra contain a single characteristic absorption maximum which shifts predictably as the electronegative groups are varied. The reaction of malononitrile with trifluoroacetonitrile

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[1] V. Migrdichian, "The Chemistry of Organic Cyanogen Compounds," Reinhold Publishing Corp., New York, N. Y., 1947, p. 285.

[2] S. Baldwin, *J. Org. Chem.*, **26**, 3288 (1961), and references cited therein.