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Concerted Mechanisms of the Reactions of Methyl Aryl Carbonates with Substituted Phenoxide Ions

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The reactions of 4-nitrophenyl, 2,4-dinitrophenyl, and 2,4,6-trinitrophenyl methyl carbonates (NPC, DNPC, and TNPC, respectively) with substituted phenoxide ions are subjected to a kinetic study in water at 25.0 °C, ionic strength 0.2 M (KCl). Production of the leaving groups (the nitro derivatives) is followed spectrophotometrically. Under excess of the phenoxide ions pseudo-first-order rate coefficients (k_{obsd}) are found throughout. Plots of k_{obsd} vs substituted phenoxide concentration at constant pH are linear, with the slope (k_N) independent of pH. The Brönsted-type plots (log k_N vs pK_a of the phenols) are linear with slopes $\beta = 0.67$, 0.48, and 0.52 for the phenolysis of NPC, DNPC, and TNPC, respectively. The magnitudes of these Brönsted slopes are consistent with a concerted mechanism. In the particular case of the phenolysis of NPC the expected hypothetical curvature center of the Brönsted plot for a stepwise mechanism should be p$K_a{}^0 = 7.1$ (the pK_a of 4-nitrophenol). This curvature does not appear within the pK_a range of the substituted phenols studied (5.3−10.3), indicating that these reactions are concerted. The phenolysis of DNPC and TNPC should also be concerted in view of the even more unstable tetrahedral intermediates that would be formed if the reactions were stepwise. The reactions of the same substrates with pyridines are stepwise, which means that substitution of a pyridine moiety in a tetrahedral intermediate by a phenoxy group destabilizes the intermediate perhaps to the point of nonexistence. The k_N values for the title reactions are larger than those for the concerted phenolysis of the corresponding ethyl *S*-aryl thiolcarbonates. The k_N values found in the present reactions are subjected to a dual regression analysis as a function of the pK_a, of both the nucleophile and leaving group, the coefficients being $\beta_N = 0.5$ and $\beta_{lg} = -0.3$, respectively. These coefficients are consistent with a concerted mechanism.

Introduction

The kinetics and mechanisms of the aminolysis and pyridinolysis of carboxylic acid derivatives, such as esters and carbonates, have been extensively investigated.[1−4] Nevertheless, the mechanisms of the reactions of phenoxide anions with these substrates have been much less studied.[5]

In the present work we undertake a kinetic and mechanistic study of the reactions of phenoxide anions with methyl 4-nitrophenyl, methyl 2,4-dinitrophenyl, and methyl 2,4,6-trinitrophenyl carbonates with the purpose of clarifying the mechanisms of the phenolysis of aryl carbonates. In this paper we also compare these mechanisms with those for the pyridinolysis of the same substrates[3] and the phenolysis of other carboxylic derivatives[5] and thiolcarbonates.[6]

Experimental Section

Materials. The substituted phenols (Aldrich) were purified either by distillation or recrystallization. The substrates were synthesized as previously reported.[3] Methyl phenyl carbonate (one of the products from the reactions of the substrates with phenoxide anion) was prepared as described previously.[4a]

Determination of pK_a. The pK_a values of 3-chloro and 2,6-difluoro phenols were determined spectrophotometrically, at 239 and 232 nm, respectively, in water at 25.0 ± 0.1 °C, ionic strength 0.2 M (KCl), by the method described.[7] The pK_a determination of the other phenols has been reported previously.[8]

Kinetic Measurements. The reactions were followed spectrophotometrically in the range 300−500 nm (appearance of

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Table 1. Experimental Conditions and k_{obsd} Values for the Reactions of Phenoxide Anions with Methyl 4-Nitrophenyl Carbonate (NPC)[a]

phenoxide substituent	pH	F_N [b]	10^3 [phenol]$_{tot}$ [c] (M)	10^4 k_{obsd} (s^{-1})	no. of runs
4-MeO	10.0	0.33	1.0−40	12.0−359	7
	10.3	0.50	1.0−40	34.3−502	8
	10.6	0.66	1.0−40	53.0−542	8
H	9.6	0.33	1.0−40	4.79−100	8
	9.9	0.50	2.5−40	8.66−168	7
	10.2	0.66	2.5−40	14.4−204	7
3-Cl	8.7	0.33	4.0−40	5.74−53.7	6
	9.0	0.50	1.0−40	2.66−68.7	8
	9.3	0.66	1.0−40	4.00−89.6	8
4-CN	7.5	0.33	6.0−80	0.391−7.40	7
	7.8	0.50	4.0−80	0.462−11.6	8
	8.1	0.67	4.0−80	0.848−15.7	8
2,6-F_2	6.8	0.33	8.0−40	0.42−1.72	4
	7.1	0.50	8.0−40	0.68−2.29	4
	7.4	0.66	8.0−40	0.768−3.15	4
2,3,4,5,6-F_5	8.0 [d]	1.00	8.0−80	0.308−1.04	6

[a] In aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl). [b] Free phenoxide fraction of total phenol. [c] Total concentration of substituted phenol (acid plus conjugate base). [d] In the presence of borate buffer 0.01 M.

Table 2. Experimental Conditions and k_{obsd} Values for the Reactions of Phenoxide Anions with Methyl 2,4-Dinitrophenyl Carbonate (DNPC)[a]

phenoxide substituent	pH	F_N [b]	10^3 [phenol]$_{tot}$ [c] (M)	10^4 k_{obsd} (s^{-1})	no. of runs
4-MeO	10.0	0.33	1.0−40	7.93−168	7
	10.3	0.50	1.0−40	13.4−226	8
	10.6	0.67	2.5−40	30.1−268	7
H	9.6	0.33	1.0−40	2.0−49.8	8
	9.9	0.50	1.0−40	3.66−76.0	8
	10.2	0.67	1.0−40	6.14−112	8
3-Cl	8.7	0.33	1.0−40	0.67−33.2	8
	9.0	0.50	1.0−40	1.14−44.9	8
	9.3	0.67	1.0−40	1.90−57.2	8
4-CN	7.5	0.33	4.0−40	0.60−5.80	6
	7.8	0.50	2.5−40	0.55−6.72	7
	8.1	0.67	2.5−40	0.741−11.5	7
2,6-F_2	6.8	0.33	8.0−40	0.882−4.85	4
	7.1	0.50	1.0−40	0.207−7.02	8
	7.4	0.67	1.0−40	0.25−9.33	8
2,3,4,5,6-F_5	8.0 [d]	1	4.0−80	0.201−2.39	8
	8.5 [d]	1	4.0−80	0.225−2.86	8
	9.0 [d]	1	4.0−80	0.29−3.0	8

[a] In aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl). [b] Free phenoxide fraction of total phenol. [c] Total concentration of substituted phenol (acid plus conjugate base). [d] In the presence of borate buffer 0.01 M.

Table 3. Experimental Conditions and k_{obsd} Values for the Reactions of Phenoxide Anions with Methyl 2,4,6-Trinitrophenyl Carbonate (TNPC)[a]

phenoxide substituent	pH	F_N [b]	10^3 [phenol]$_{tot}$ [c] (M)	10^4 k_{obsd} (s^{-1})	no. of runs
H	9.9	0.50	0.8−8.0	2.0−9.2	5
	10.2	0.66	0.8−8.0	0.86−3.9	6
3-Cl	8.7	0.33	1.0−40	0.67−6.1	6
	9.0	0.50	4.0−40	0.80−8.4	6
	9.3	0.66	4.0−40	1.30−10.1	6
4-CN	7.5	0.33	10−400	0.15−5.24	8
	7.8	0.50	10−400	0.20−7.0	8
	8.1	0.67	10−400	0.29−10.7	8
2,6 −F_2	6.8	0.33	80−400	0.108−3.5	4
	7.1	0.50	10−400	0.195−4.79	8
	7.4	0.67	10−400	0.40−4.35	7
2,3,4,5,6-F_5	8.0 [d]	1	40−800	0.233−3.6	8
	8.5 [d]	1	40−800	0.211−3.65	8
	9.0 [d]	1	40−800	0.23−3.70	8

[a] In aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl). [b] Free phenoxide fraction of total phenol. [c] Total concentration of substituted phenol (acid plus conjugate base). [d] In the presence of borate buffer 0.01 M.

Table 4. Values of pK_a of Phenols and k_N for the Phenolysis of Methyl Aryl Carbonates[a]

phenoxide substituent	pK_a	k_N (s^{-1} M^{-1}) NPC	DNPC	TNPC
4-MeO	10.3 [b]	2.23 ± 0.05	11.1 ± 0.5	
H	9.9 [b]	0.77 ± 0.01	3.9 ± 0.1	87 ± 5
3-Cl	9.0	0.33 ± 0.01	2.2 ± 0.1	39 ± 1
4-CN	7.8 [b]	0.029 ± 0.001	0.41 ± 0.02	3.8 ± 0.1
2,6-F_2	7.1	0.011 ± 0.0005	0.35 ± 0.02	1.8 ± 0.1
2,3,4,5,6-F_5	5.3 [b]	0.001 ± 0.0002	0.033 ± 0.002	0.45 ± 0.02

[a] Both the pK_a and k_N values were determined in aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl). [b] Values taken from ref 6.

the leaving nitrophenoxide anions) by means of a Hewlett-Packard 8453 diode array spectrophotometer. All reactions were studied in aqueous solution at 25.0 ± 0.1 °C, ionic strength 0.2 M (KCl). In most cases, the substituted phenol and its conjugate base acted as buffer, and in a few cases, the buffer was borate 0.01 M.

In all cases the initial substrate concentration was 2×10^{-5} M, and the substituted phenol was at least in a 10-fold excess over the substrate.

Under these conditions, pseudo-first-order rate coefficients (k_{obsd}) were found by fitting of the first-order rate equation to the experimental points; nevertheless, for the slowest reactions (the mononitro substrate with 2,6-difluoro and pentafluoro phenols) the initial rate method was used.[5b] The experimental conditions of the reactions and the k_{obsd} values are shown in Tables 1−3.

Product Studies. For the phenolysis of the 4-nitro, 2,4-dinitro, and 2,4,6-trinitro substrates one of the products was identified as 4-nitrophenoxide, 2,4-dinitrophenoxide, and 2,4,6-trinitrophenoxide ions, respectively. The identification was achieved by comparison of the UV−vis spectra after completion of the reactions with those of authentic samples under the same conditions. The reactions of unsubstituted phenoxide ion with the three substrates yield methyl phenyl carbonate as the other product of the reactions, as indicated by comparison of the HPLC spectrum of an authentic sample with those obtained after completion of the reactions. HPLC conditions: column, Eurospher C-18 (10 cm, 7 μm); eluant, acetonitrile/water = 70/30; isocratic mode, 0.7 mL/min.

Results and Discussion

The phenolyses of the title substrates are governed kinetically by eq 1, where k_{obsd} is a pseudo-first-order rate

$$k_{obsd} = k_o + k_N [ArO^-] \qquad (1)$$

coefficient, k_o and k_N are the rate coefficients for hydrolysis and phenolysis, respectively, and ArO^- represents the nucleophile, a substituted phenoxide ion. The values of k_o and k_N were obtained as the intercept and slope, respectively, of linear plots of k_{obsd} vs $[ArO^-]$ at constant pH.

For almost all the reactions the values of k_o and k_N are independent of pH. Only for the reaction of methyl 2,4-dinitrophenyl carbonate (DNPC) with pentafluorophenoxide anion was there observed an increase of the k_o value with the increase of pH.

Table 4 shows the k_N values obtained in the present reactions and the pK_a values of the phenols found under the same experimental conditions as those of the kinetic measurements. The Brönsted-type plots obtained with the k_N values for the phenolysis of the three substrates are shown in Figure 1. These plots are linear with slopes

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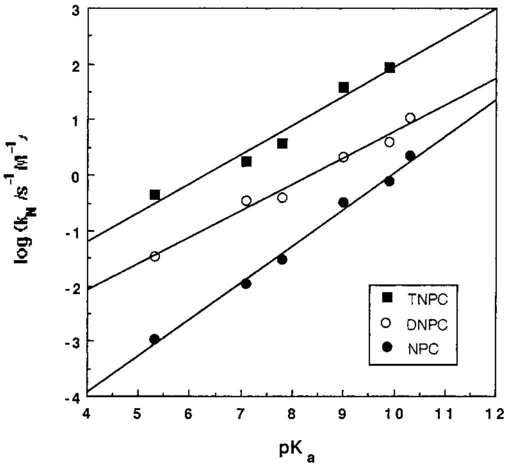

Figure 1. Brönsted-type plots obtained in the phenolysis of 4-nitrophenyl, 2,4-dinitrophenyl, and 2,4,6-trinitrophenyl methyl carbonates (NPC, DNPC, and TNPC, respectively) in aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl).

$\beta = 0.67 \pm 0.03$, 0.48 ± 0.03, and 0.52 ± 0.06 for the reactions of 4-nitrophenyl, 2,4-dinitrophenyl, and 2,4,6-trinitrophenyl methyl carbonates, respectively (NPC, DNPC, and TNPC, respectively).

The fact that these Brönsted plots are linear is in contrast with the sharp breaks found in the Brönsted plots for the phenolysis of bis(4-nitrophenyl) phenylphosphonate in water and in water/dimethyl sulfoxide mixtures.[9] These Brönsted breaks, centered at pK_a values much larger than that of 4-nitrophenol, cannot be explained by a stepwise mechanism (through a pentacoordinate intermediate) and a change in rate-determining step.[9] The breaks were attributed to the occurrence of solvational imbalance phenomena in the transition state of the reactions.[9] Nevertheless, these Brönsted breaks are not observed in the reactions of the present work (Figure 1) nor in the phenolyses of ethyl *S*-aryl thiolcarbonates,[6] aryl chlorothionoformates,[8] aryl acetates,[5b,d] 4-nitrophenyl diphenylphosphinate, and 4-nitrophenyl diphenyl phosphate.[10]

The values of the Brönsted slopes obtained in the title reactions are in agreement with those found in the concerted reactions in water of phenoxide ions with aryl esters and analogous carboxylic derivatives, such as 1-acetoxy-8-hydroxynaphthalene ($\beta = 0.48$),[11] 4-chloro 2-nitrophenyl acetate ($\beta = 0.64 \pm 0.05$),[5d] acetic anhydride ($\beta = 0.58 \pm 0.05$),[12] 2,4-dinitrophenyl acetate ($\beta = 0.57 \pm 0.03$),[12] 3-nitrophenyl, 4-nitrophenyl, and 3,4-dinitrophenyl formates (β = 0.64, 0.51, and 0.43, respectively),[5e] and the corresponding acetates ($\beta = 0.66$, 0.59, and 0.53, respectively).[5e]

On the other hand, concerted phenolyses of carboxylic compounds in water with larger Brönsted slopes ($\beta = 0.8-1$) have also been reported.[5d] Even larger β values have been found in the reactions of phenoxide anions with acetic anhydride in solvents less polar than water, e.g., $\beta = 1.3$ and 1.6 in acetonitrile and chlorobenzene, respectively.[13]

Clearly, the magnitude of the Brönsted slope alone is not sufficient to decide whether the mechanism is concerted or stepwise. A proof for a stepwise reaction (through a tetrahedral intermediate) would be to observe a Brönsted break (due to change in the limiting step) centered at the pK_a of the leaving group, provided the attacking and leaving groups are of the same nature.[14,15]

If the phenolysis of NPC were stepwise the hypothetical break of the Brönsted-type plot would be at pK_a = 7.1, which is the pK_a of 4-nitrophenol in water. The pK_a range of the conjugate acids of the nucleophiles, i.e., substituted phenols, covered in this work is 5.3−10.3. Since no break is observed in the Brönsted plot for NPC in Figure 1, it can be concluded that the mechanism for the phenolysis of NPC is concerted.

For the phenolyses of DNPC and TNPC the hypothetical Brönsted breaks for stepwise mechanisms are outside the pK_a range of the phenols, in view of the low pK_a of 2,4-dinitro- and 2,4,6-trinitro phenols (pK_a 4.0 and 0.33, respectively).[7] If these reactions were stepwise, formation of the tetrahedral intermediate would be rate-determining, since expulsion of the leaving groups from the intermediate would be much faster than that for the attacking phenoxide ions. The Brönsted slopes obtained for these reactions (Figure 1) are larger than the usual β values found for similar reactions when formation of the tetrahedral intermediate is the rate-limiting step ($\beta = 0.1-0.3$).[1,2,5a,15,16] This analysis indicates that the reactions of DNPC and TNPC are concerted.

Another reason to believe that the phenolyses of DNPC and TNPC are governed by concerted mechanisms is the fact that the same reaction of NPC is concerted. If the hypothetical intermediate that would be formed in the reactions of NPC (if the mechanism were stepwise) is either too unstable to exist (enforced concerted process) or very unstable but existent,[14,17] the change of 4-nitrophenoxy to 2,4-dinitro- or 2,4,6-trinitrophenoxy would render the intermediate even more unstable. Therefore, it is reasonable that the phenolyses of DNPC and TNPC are also concerted.

The reactions of the title substrates with pyridines in aqueous solution are stepwise, with the formation of a zwitterionic tetrahedral intermediate ($T^{\pm}$).[3] This conclusion arises from the large slope value of the linear Brönsted plot for the pyridinolysis of NPC,[3a] and the biphasic behavior of the Brönsted plots in the reactions of DNPC[3b] and TNPC.[3c] The former result was explained by the breakdown of $T^{\pm}$ to products as being rate-limiting.[3a] The biphasic Brönsted plots for the pyridinolyses of DNPC and TNPC were interpreted through a change in rate-determining step, from breakdown to formation of $T^{\pm}$, as the nucleophile becomes stronger.[3b,c]

The fact that the pyridinolyses of the title substrates are stepwise, whereas their phenolyses are concerted, means that the tetrahedral intermediates in the former reactions are much destabilized by the change of a pyridine to a phenoxy group.

This is consistent with the fact that the pyridinolyses of aryl acetates,[1,3c,4a,18] aryl benzoates,[19] ethyl *S*-aryl

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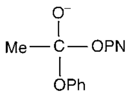
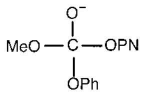
thiolcarbonates,[20] and acetic anhydride[21] are stepwise, whereas the phenolyses of the same substrates are concerted.[5b,d,f,6,12]

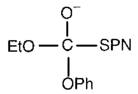
Since the reactions of phenoxide ions with 4-nitrophenyl acetate are concerted, the tetrahedral "intermediate" **1** (PN = 4-nitrophenyl) either does not exist or is very unstable.[5b] On the other hand, it is known that the change of methyl by a methoxy group destabilizes the tetrahedral intermediate;[22] therefore the "intermediate" **2** should be even more unstable than **1**. This indicates that the phenolysis of NPC should be concerted, as found in the present work.



$\mathrm{Me{-}C(O^-)(OPh){-}OPN}$



$\mathrm{MeO{-}C(O^-)(OPh){-}OPN}$



$\mathrm{EtO{-}C(O^-)(OPh){-}SPN}$

The phenolysis of ethyl *S*-(4-nitrophenyl) thiolcarbonate was found to be driven by a concerted mechanism.[6] This means that structure **3** should also be very unstable. On the other hand, the change of a methoxy group by ethoxy should not significantly affect the stabilization of a tetrahedral intermediate.[23] The change of 4-nitrophenoxy to 4-nitrobenzenethio should stabilize slightly structure **3**,[6] despite the relatively large difference of the basicities involved (pK_a values of their conjugate acids 7.1 and 4.6, respectively), which would suggest that SPN should leave faster than OPN. Nonetheless, it should be taken into account that phenoxides are better nucleofuges than *isobasic* benzenethiolates from tetrahedral structures.[24]

The nucleophilic rate constants (k_N) found in this work are larger than those obtained in the concerted phenolysis of the corresponding ethyl *S*-aryl thiolcarbonates.[6] This result is in accord with the larger k_N values found in the concerted reactions of secondary alicyclic amines with TNPC[25] compared with ethyl *S*-(2,4,6-trinitrophenyl) thiolcarbonate.[26b] Also in line are the results in stepwise aminolyses: (i) the pyridinolyses of NPC, DNPC, and TNPC are faster[3] than those of the corresponding ethyl *S*-aryl thiolcarbonates,[20] (ii) anilines are more reactive toward DNPC than ethyl *S*-(2,4-dinitrophenyl) thiolcarbonate,[26d] and (iii) quinuclidines react faster with phenyl 4-nitrophenyl carbonate[2] than ethyl *S*-(4-nitrophenyl) thiolcarbonate.[26c] This difference in reactivity presumably arises from the bulkier *S* atom, relative to the *O* atom, which inhibits the attack to the thiolcarbonates by the nucleophile.

With the k_N values found in the present reactions together with the pK_a values for both the nucleophiles and leaving groups (Table 4), eq 2 can be deduced by dual regression analysis ($n = 17$, $R^2 = 0.97$). In this expression N and lg refer to nucleophile and leaving group, respectively; the pK_a coefficients ($\beta_N = 0.5$ and $\beta_{lg} = -0.3$) are subjected to an error of ± 0.1.

$$\log k_N = -3.2 + 0.5\ \mathrm{p}K_a(\mathrm{N}) - 0.3\ \mathrm{p}K_a(\mathrm{lg}) \qquad (2)$$

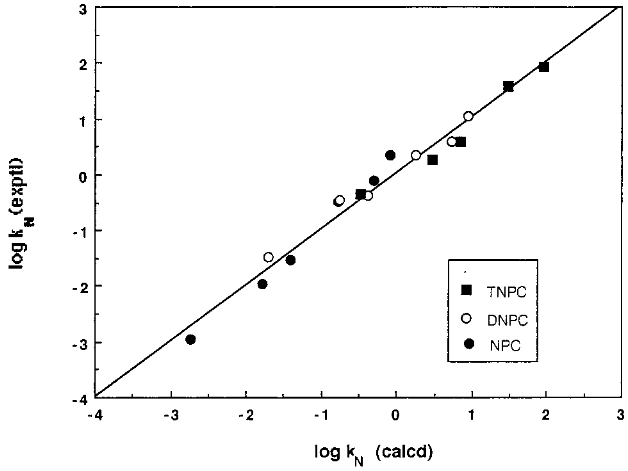


Figure 2. Logarithmic plot of experimental k_N vs calculated k_N (through eq 2) for the phenolysis of methyl aryl carbonates in aqueous solution at 25.0 °C, ionic strength 0.2 M (KCl).

A logarithmic plot of the experimental k_N vs the calculated one through eq 2 is shown in Figure 2; the slope is unity.

The sensitivity of k_N to the nucleophile ($\beta_N = 0.5$) is in agreement with those exhibited in several phenolysis when the reaction mechanism is concerted, as was mentioned earlier.[5a,e,11,12] For the concerted aminolysis (secondary alicyclic amines, anilines and quinuclidines) of carbonates and similar compounds in water the value of β_N is 0.5−0.6.[15,17b,22,26]

On the other hand, the sensitivity of k_N to the leaving group basicity ($\beta_{lg} = -0.3$) is in agreement with those exhibited in the concerted aminolysis of ethyl *S*-aryl thiolcarbonates in water ($\beta_{lg} = -0.19$)[26b] and the concerted phenolysis of aryl formates (β_{lg} from −0.31 to −0.48),[5e] although smaller than those obtained in the concerted phenolysis of aryl acetates (β_{lg} from −0.50 to −0.63).[5e]

The values of the rate constants for the phenolyses of 4-nitrophenyl and 2,4-dinitrophenyl acetates[5d,e] are larger than those found for the reactions of the same nucleophiles with NPC and DNPC, respectively (this work). In other words, substitution of Me by MeO lowers the k_N value, as found in the stepwise aminolyses of these substrates.[3a,b,4a] This can be explained by the larger electron-releasing effect exerted by MeO compared to that of Me, which inhibits amine attack to the carbonyl center[3a] decreasing, therefore, the rate constants for both the stepwise and concerted mechanisms.

The k_N values for the phenolysis of 4-nitrophenyl formate are larger than those for the same reactions of NPC. This can be accounted for by the lower steric hindrance and the absence of an electron-releasing effect by the formate esters.[5e]

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