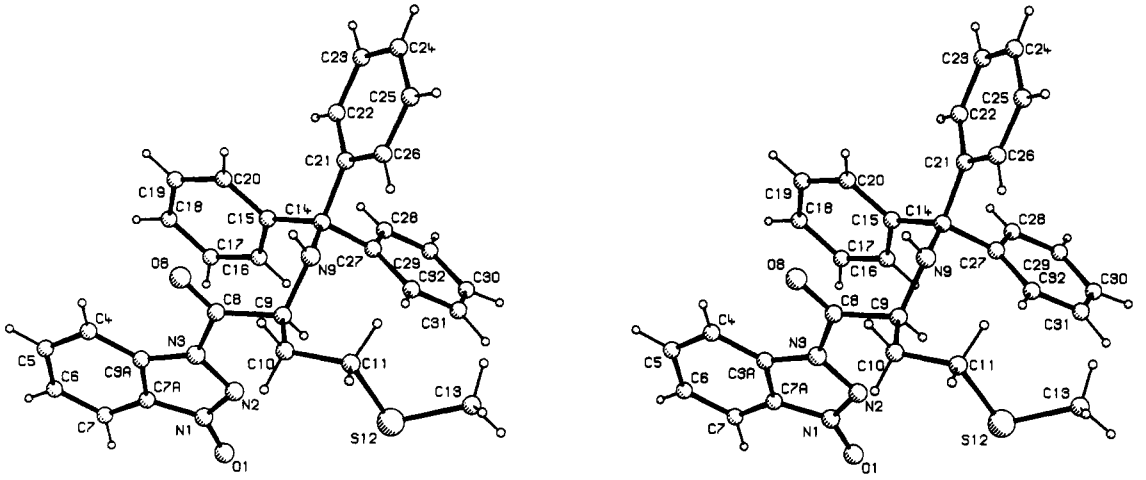

Figure 1. Stereoscopic view of the molecule with atomic numbering.

Table I. Bond Lengths (angstroms) and Bond Angles (degrees) with Standard Deviations in Parentheses

N(1)–O(1)	1.267 (2)	N(3)–C(3a)	1.393 (3)
N(1)–N(2)	1.311 (2)	N(3)–C(8)	1.412 (2)
N(1)–C(7a)	1.411 (3)	C(3a)–C(7a)	1.384 (3)
N(2)–N(3)	1.385 (2)		
O(1)–N(1)–N(2)	122.6 (2)	N(2)–N(3)–C(8)	120.4 (2)
O(1)–N(1)–C(7a)	124.9 (2)	N(3)–C(3a)–C(7a)	105.4 (2)
N(1)–N(2)–N(3)	105.0 (1)	N(3)–C(3a)–C(4)	133.6 (2)
N(1)–C(7a)–C(3a)	105.8 (2)	C(3a)–N(3)–C(8)	127.8 (2)
N(1)–C(7a)–C(7)	130.2 (2)	C(3a)–C(7a)–C(7)	123.9 (2)
N(2)–N(1)–C(7a)	112.5 (2)	C(4)–C(3a)–C(7a)	121.0 (2)
N(2)–N(3)–C(3a)	111.2 (1)		

crystallographic investigation on the well crystalline *N*-(N^{α}-tritylmethionyl)benzotriazole 1-oxide, exhibiting an IR carbonyl band at 1730 cm^{-1}.

The stereoscopic drawing of the examined compound as it is revealed by the crystallographic analysis is shown in Figure 1. Bond lengths and bond angles for the triazole ring are presented in Table I. The present X-ray analysis conclusively demonstrates that the methionyl moiety is attached at N3. Thus, the benzotriazolyl derivatives of N^{α}-protected amino acids in the amide form, with IR carbonyl absorbance in the region 1730–1750 cm^{-1}, must have the structure **2b** and not the structure **2a**. Moreover, although construction **2b** excludes the proximity of the basic oxygen atom (O1) on the benzotriazole ring, and the H atom (H9) of the chiral C atom, it places H9 very close to the second basic atom (N2) of the same ring. Indeed, the distance H9···N2 is ca. 2.38 Å, almost close enough to be considered a C–H–N hydrogen bond, if the CHN angle were straighter.

We therefore conclude that the extent of racemization through intramolecular direct hydrogen abstraction must depend not only on purely electronic considerations but also on steric factors which impose the possible proximity of the H atom (H9) of the chiral C atom and the central N atom (N2) of the benzotriazole ring.

X-ray Diffraction Analysis

Colorless crystals of 3-(N^{α}-tritylmethionyl)benzotriazole 1-oxide, $C_{30}H_{28}N_4O_2S$, were grown from acetone after recrystallization from diethyl ether/petroleum ether (60–80 °C). Crystals grown from acetone also showed the usual IR carbonyl absorption band at 1730 cm^{-1}. The space group is $P2_12_12_1$, a = 8.7008 (5) Å, b = 14.3777 (15) Å, c = 20.846 (3) Å, Z = 4, at ca. 130 K. Within (sin θ/λ = 0.74, 4838 unique reflections were measured on a Nicolet-R3 diffractometer with cooling device LT-1. The structure was solved by the heavy atom method and refined by a blocked-cascade least-squares refinement (ca. 100 variables per block). The H atoms were refined with individual isotropic temperature factors after their location in a difference Fourier map while the other atoms were varied anisotropically. The 446 variables converged at R = 0.064 by using all unique reflections.

Registry No. 3-(N^{α}-tritylmethionyl)benzotriazole 1-oxide, 93984-96-4; N^{α}-tritylmethionine benzotriazolyl ester, 93984-97-5.

Supplementary Material Available: Details of data collection and structure refinement, tables of atomic parameters and thermal vibration parameters, and complete tables of bond lengths and bond angles (7 pages). Ordering information is given on any current masthead page.

Selective Decarbethoxylation of Ethyl 1,4-Dimethyl-3-(ethoxycarbonyl)-1*H*-pyrrole-2-acetate in 85% Phosphoric Acid

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Decarboxylation of pyrrolecarboxylic acids is an important step in the synthesis of substituted pyrroles, giving intermediates for electrophilic substitution at vacated sites on the pyrrole ring.[1] Heating of some ethyl pyrrolecarboxylates or acyl pyrroles in 85% phosphoric acid results in decarbethoxylation or cleavage of acyl groups from the starting pyrrole molecule.[2,3] It was assumed that both decarbethoxylation and acyl cleavage proceed by the same mechanism involving a protonated pyrrole (Scheme I).[3]

However, the competitive route of hydrolysis and subsequent decarboxylation of the pyrrolecarboxylic acid may also be operative. This pathway was actually demonstrated by treating **1** (Chart I and II) in a mixture of 96% sulfuric acid, ethanol, and water.[4] In this medium intermediate

(1) Gossauer, A. "Die Chemie der Pyrrole"; Springer-Verlag: Berlin, 1974; p 257.
(2) Treibs, A.; Schulze, L. *Liebigs Ann. Chem.* **1970**, *739*, 225.
(3) Finizio, M.; Schoen, K. *Farmaco*, Ed. Sci. **1972**, *27*, 621.
(4) Stahly, G. P.; Marlett, E. M.; Nelson, G. E. *J. Org. Chem.* **1983**, *48*, 4423.

0022-3263/85/1950-0697$01.50/0

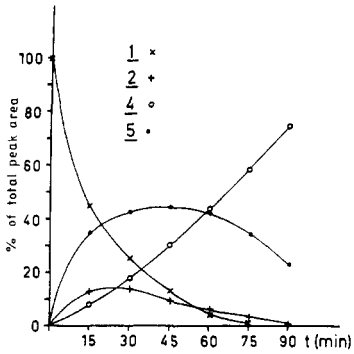
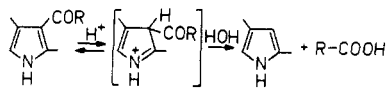


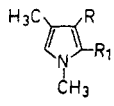
Figure 1. GC-monitored conversion of 1 in 85% phosphoric acid at 80 °C.

Scheme I



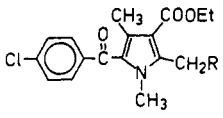
R = Me, OEt

Chart I



R	R_1	Compd.
COOEt	CH_2COOEt	1
COOEt	CH_2COOH	2
COOH	CH_2COOH	3
H	CH_2COOH	4
H	CH_2COOEt	5
COOH	CH_2COOEt	6
COOEt	Me	7
H	Me	8

Chart II



R	Compd.
COOEt	9
COOH	10
H	11

monoacids **2** and **6** were detected, and underwent decarboxylation to **5**, **7**, and **8**. This paper prompted us to report our investigation of the selective conversion of **1** to **5** in phosphoric acid which proceeds by different reaction pathways.

Heating **1** for 10 min in 85% phosphoric acid at 90 °C produced **5** in a 34% isolated yield. Results of GC monitoring at 80 °C (Figure 1) revealed a profile consistent with at least two parallel pathways, one resulting in the fast formation of **5** in the initial period and another leading to **4**, presumably via the intermediate **2**. The monoacid **2** can be isolated from the reaction mixture after heating for 20 min at 80 °C. However, neither of the possible intermediates **3** and **6** was detected by GC, nor were the decarboxylated products **7** and **8** (see Experimental Section).

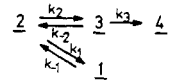
In separate experiments, conversions of compounds **1–3** and **6** at different temperatures and concentrations of phosphoric acid were monitored by GC (Table I). Compounds **3** and **6** underwent fast decarboxylation on heating in concentrated or dilute phosphoric acid, while **1** gave only the monoacid **2** in 85% or 28% phosphoric acid. Under the latter conditions, **4** and **5** would be produced if **3** and/or **6** were formed from **1**. Since this was not the case, one can conclude that the 3-ethoxycarbonyl group in **1** hydrolyzes much slower than the acetate group in the 2 position. Consequently, the fast formation of **5** shown in Figure 1 probably reflects direct decarbethoxylation rather than the decarboxylation of previously formed monoacid **6**.

Table I. GC-Determined Compositions of the Reaction Mixtures from Reactions of Compounds 1, 2, 3, and 6 in Phosphoric Acid

starting compd	reactn time, min	reactn temp, °C	H_3PO_4, %	compositn of the reactn mixture, % of total			
				1	2	4	5
1	2 days	RT[a]	85	88.0	11.9		
1	45	80	28	61.5	38.2		
2	25	80	85		9.7	67.5	9.7
3	10	60	85			93.7	
3	45	80	28			100.0	
6	5	50	85				92.2
6	45	80	28			72.5	24.9

[a] RT = room temperature.

Scheme II



The selective hydrolysis of the 2-acetate group observed with **1** also occurred with the 5-*p*-chlorobenzoyl-substituted pyrrole **9**. Thus heating **9** for 1 h in 85% phosphoric acid at 80 °C produced 65% of monoacid **10**.[5,7] Increasing the reaction temperature to 90 or 100 °C resulted in extensive formation of *p*-chlorobenzoic acid, which was isolated in 60% yield after 1 h. Here the debenzoylation reaction is competitive with decarbethoxylation of the 3-ethoxycarbonyl group. After cleavage of the *p*-chlorobenzoyl group, the remaining pyrrole molecule decomposed readily; a TLC control showed several red spots.

The intermediate monoacid **2** was converted mainly into **4** by heating at 80 °C for 25 min (Table I), supporting the assumption that **2** could be an intermediate in the conversion of **1** to **4**. Most of **4** is probably formed by hydrolysis of **5** (Figure 1). In the conversion of **2** to **4**, about 10% of **5** was formed, presumably by esterification of **4** with ethanol evolved in the decarbethoxylation step. The possibility of partial esterification in 85% phosphoric acid at a very unfavorable ethanol:water ratio was demonstrated by heating a 0.073 M solution of phenylacetic acid and ethanol in 85% phosphoric acid at 80 °C for 45 min, which produced 17% of ethyl phenylacetate as determined by GC.

In addition, one of the possible reaction pathways for the conversion of **2** to **4** (Scheme II) was tested by following the disappearance of **2** by GC at 61 °C in 84.6% phosphoric acid. First-order dependence was obtained at initial concentrations of 0.044 M and 0.022 M of **2**, giving k_{obsd} of 9.8 and 8.8×10^{-5} s^{-1}, respectively. To test the possible formation of **1**, a preliminary experiment was performed in which **2** was heated with 2 equiv of ethanol. Since no **1** was detected by GC, k_1 must be very low in comparison to k_2 and k_3. Furthermore, $k_3 > k_2$ if the reaction pathway shown in Scheme II holds, since fast decarboxylation of **3** to **4** was found (Table I). Consequently, the hydrolysis of **2** into **3** would be the slower step in the overall transformation of **2** into **4**, which would be considerably affected

(5) This reaction was directed to the one-step formation of 1,4-dimethyl-5-(*p*-chlorobenzoyl)-1*H*-pyrrole-2-acetic acid, a new potent antiinflammatory agent.[6]

(6) Carson, J. R.; Wong, S. *J. Med. Chem.* **1973**, *16*, 172.

(7) The structure of **10** is proved by the ^{13}C NMR spectrum, $CDCl_3$, (δ and off-resonance multiplets given): 187.2 (s), 173.5 (s), 165.8 (s), 139.2 (s), 138.0 (s), 137.0 (s), 131.5 (d), 130.1 (s), 129.0 (s), 128.9 (d), 113.6 (s), 60.4 (t), 32.7 (q), 32.0 (t), 14.3 (q), 13.9 (q). The signal at 173.5 ppm is split into a long-range triplet ($^2J_{C,H}$ = 8.1 Hz). Additional proof for the structure of **10** was obtained by heating it for 2 h at 210–230 °C and decarboxylating it to **11**.

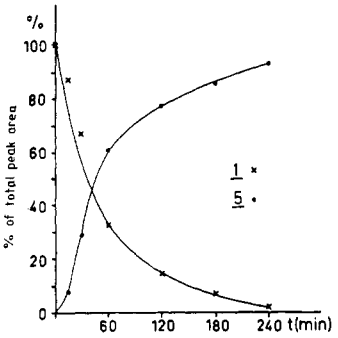
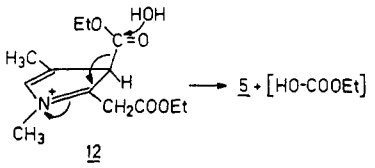


Figure 2. GC-monitored conversion of 1 to 5 by heating in 100% phosphoric acid at 80 °C.

Scheme III



12

by the addition of ethanol. However, the presence of 0.088 M ethanol in the 0.044 M solution of **2** in 84.6% phosphoric acid produced no effect on k_{obsd} (9.8×10^{-5} s^{-1}), suggesting that the intermediacy of **3** is unlikely.

Thus, both kinetic evidence and qualitative experiments support the direct decarbethoxylation of **1** and **2** without prior hydrolysis to the acid. Figure 2 shows that direct decarbethoxylation occurred under anhydrous conditions to give **5** in 97% (GC) yield.

A striking difference between the reaction pathways for the conversion of **1** to **5** in a strongly acidic mixture of 96% sulfuric acid, ethanol, and water (10:9:1)[4] and in 85% phosphoric acid is demonstrated by the presence of monoacid intermediates **2** and **6** in the former and only **2** in the latter. Decreased reactivity of the 3-ethoxycarbonyl group in **1** and **2** toward hydrolysis in phosphoric acid may be the result of steric hindrance in the rate-determining, nucleophilic attack of a water molecule ($A_{AC}2$ mechanism[8,9]). The carbonyl group in the 3 position of **1** and **2** would be almost perpendicular to the plane of the pyrrole ring, as suggested by MNDO calculations for acetylmesitylene and 2,6-dimethylacetophenone.[11] Consequently, the attack of a water molecule is hindered by the substituents in the 2 and 4 positions. On the other hand, protonation of the pyrrole ring would be expected in concentrated phosphoric acid,[12,13] leading to the protonated pyrrole **12** (Scheme III) with the 3-ethoxycarbonyl group situated above or below the plane of the pyrrole ring. The nucleophilic attack of a water molecule on the carbonyl carbon in the 3 position of **12** is not hindered, and substitution of the protonated pyrrole is favored since it is a better leaving group than ethoxide ion.[15] However, in a strongly acidic medium[4] protonation of both the 3-ethoxycarbonyl group and the pyrrole ring is likely to occur, which may account for the observed hydrolysis to the intermediate monoacid **6**.

Experimental Section

Materials. Compounds **1**, **3**–**6**, and **7** were prepared by published procedures.[4,6]

Equipment. Gas chromatograms and IR spectra were recorded on instruments manufactured by PYE UNICAM, Cambridge; GC 204 with a CDP4 computing integrator and Grob injector; IR spectrophotometer SP3-200. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer with Me_4Si as internal standard. Melting points were determined on a Kofler heating stage and are uncorrected.

General Methods. The GC column (27 m × 0.31 mm i.d.) was made of Duran 126 glass tubing. Grob's procedures were used for preparing[16,17] and testing[19] the column, which was coated with OV-1 5‰ in dichloromethane.[18] Instrument conditions were as follows: temperature program 120–260 °C at a rate of 6°/min; initial time 2 min; final time of analysis 4 min; injector temperature 300 °C; detector temperature 300 °C; detector temperature 300 °C; carrier gas was hydrogen, inlet pressure 0.5 bar. The flame ionization detector was operated with a hydrogen flow of 30 mL and an air flow of 300 mL/min. Samples were treated with ethereal diazomethane solution to convert free acids into methyl esters. Retention times (min): **1**, 12.62; **2**, 11.74; **3**, 10.80; **4**, 3.86; **5**, 4.72; **6**, 11.26; **7**, 6.74; **8**, 0.55. The sample size was 1 μL with a split ratio of 50:1.

Conversions of 1–3 and 6 in Phosphoric Acid. Compounds **1** and **3** (about 100 mg) were dissolved in 10 mL of 84.6% phosphoric acid in a volumetric flask, and 1 mL of each solution was pipetted into each of several test tubes. Similar amounts of **2** and **6** were dissolved in 10 mL of chloroform. One milliliter of each of these solutions was pipetted into each of several test tubes and evaporated to dryness with a stream of nitrogen, and to each tube was added by pipette 1 mL of phosphoric acid of the concentration shown in Table I. The test tubes were placed in a thermostated water bath at temperatures shown in Figure 1 and Table I. At appropriate time intervals the tubes were removed from the bath, diluted with 5 mL of water, and extracted with 2 mL of chloroform. From the extract 0.2 mL was pipetted and evaporated to dryness in a stream of nitrogen. The solid residue was dissolved in 0.2 mL of ethereal diazomethane solution, and after evolution of nitrogen ceased, the solution was injected into the gas chromatograph.

Since it was not possible to detect **7** and **8** by GC during the conversion of **1** (Figure 1), we assumed that they could be formed during the GC analysis when samples were not previously treated with diazomethane.[4] This was checked by reacting **1** for 30 min under the conditions given in ref 4. The chloroform extract of the reaction mixture was treated with diazomethane and analyzed by GC (compound and %): **4**, 2.1; **5**, 35.4; **6**, 3.4; **2**, 5.6; **1**, 50.8. If the chloroform extract of the reaction mixture was injected into the gas chromatograph without methylation peaks corresponding to compounds **2**, **4**, and **6** did not appear, and peaks corresponding to **7** and **8** appeared. Peak intensity for compound **5** was enhanced, indicating the thermal decarboxylation of **6** to **5**.

Conversion of 1 to 5 by Heating in 100% Phosphoric Acid. Phosphoric acid of about 100% concentration was prepared by careful dropwise addition of 10 mL of 85% phosphoric acid onto 7.2 g of P_2O_5. About 100 mg of **1** was then added and the solution

(8) Yates, K. *Acc. Chem. Res.* **1971**, *4*, 136.

(9) The hydrolysis of both ester groups in **1** would proceed by an $A_{AC}2$ rather than the $A_{AC}1$ mechanism since phosphoric acid is a weak acid. The Hammett acidity function H_0 of −3.01 for 85% phosphoric acid at 80 °C corresponds roughly to the acidity of approximately 46% sulfuric acid.[10]

(10) Rochester, C. H. "Acidity Functions"; Academic Press: London, 1970; pp 24 and 50.

(11) Anderson, A. D.; Bulbulian, R. V.; Gore, P. H.; Morris, D. F. C.; Schort, E. L. *J. Chem. Soc., Perkin Trans. 2* **1981**, 830.

(12) Chiang, Y.; Wipple, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 2763.

(13) Corwin and Straughn[14] found that 2,4,5-trimethyl-3-(ethoxycarbonyl)pyrrole can be heated in concentrated sulfuric acid at 35 °C for 45 min without hydrolysis. This was attributed to preferred protonation of the pyrrole ring; protonation of the ethoxycarbonyl group would lead to hydrolysis by an acylium ion ($A_{AC}1$) mechanism.

(14) Corwin, A. H.; Straughn, J. L. *J. Am. Chem. Soc.* **1948**, *70*, 2960.

(15) When **1** is converted to **5** in 100% phosphoric acid the phosphate anion could be the nucleophile instead of the water molecule (Scheme III). The substitution of the protonated pyrrole leads to **5** and a mixed anhydride.

(16) Grob, K. *HRC & CC, J. High Resolut. Chromatogr. Chromatogr. Commun.* **1979**, *1*, 31.

(17) Grob, K. *HRC & CC, J. High Resolut. Chromatogr. Chromatogr. Commun.* **1980**, *3*, 197.

(18) Thompson, J. C.; Schnautz, N. G. *HRC & CC, J. High Resolut. Chromatogr. Chromatogr. Commun.* **1980**, *3*, 91.

(19) Grob, K.; Grob, G.; Grob, K. *J. Chromatogr.* **1978**, *156*, 1.

heated at 80 °C with protection from moisture. At the time intervals shown in Figure 2, 0.2-mL samples were quickly taken out, diluted with 2 mL of water, and extracted with 2 mL of chloroform. One milliliter of the extract was evaporated to dryness, and the residue treated with 0.2 mL of ethereal diazomethane solution before injection into the gas chromatograph.

Preparation of 2 and 10. One gram of 1 or 9 was dissolved in 10 mL of 85% phosphoric acid and stirred under nitrogen at 80 °C for 20 min (30 min for 9). The mixture was poured onto ice and extracted with ether. The extract was washed with water and reextracted with 15 mL of 4% aqueous NaOH solution. The aqueous layer was neutralized with hydrochloric acid, and 2 or 10 separated as crystals.

2: yield 0.11 g (12%); mp 144-145 °C (2-propanol) (lit.[4] mp 154-155 °C).

10: yield 0.60 g (65%); mp 154-155 °C (2-propanol); IR (KBr) 3300-2550, 1695, 1680, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (t, 3 H), 2.00 (s, 3 H), 3.75 (s, 3 H), 4.17 (s, 2 H), 4.32 (q, 2 H), 7.59 (m, 4 H), 11.10 (br s, 1 H). Anal. Calcd for $C_{18}H_{18}NO_5Cl$: C, 59.43; H, 4.98; N, 3.85. Found: C, 59.22; H, 4.83; N, 4.00.

Preparation of 5 from 1 in 100% Phosphoric Acid. Compound 1 (2.0 g, 8.8 mmol) was dissolved in 100% phosphoric acid prepared by adding 29 mL of 85% phosphoric acid to 14.5 g of P_2O_5, and the solution was heated to 80 °C for 1 h under protection from moisture. The mixture was then poured onto ice and extracted with chloroform. The extract was dried over sodium sulfate and the chloroform evaporated under reduced pressure on a water bath at 20 °C. The residual reddish oil (1.23 g, 86%) was 95% pure (GC) and had a retention time of 4.72 min. Compound 5 is unstable and should be stored in a refrigerator.[20]

1,2,4-Trimethyl-3-(ethoxycarbonyl)-5-(*p*-chlorobenzoyl)-1*H*-pyrrole (11). One gram of 10 was decarboxylated by heating at 210-230 °C under nitrogen for 2 h. The resulting dark oil was crystallized from 2-propanol: pale yellow needles, 0.56 g (65%), mp 119-121 °C; IR (KBr) 3080, 2975, 1675, 1610, 1585 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (t, 3 H), 1.97 (s, 3 H), 2.56 (s, 3 H), 3.67 (s, 3 H), 4.28 (q, 2 H), 7.54 (m, 4 H). Anal. Calcd for $C_{17}H_{18}NO_3Cl$: C, 63.85; H, 5.67; N, 4.38. Found: C, 63.95; H, 5.68; N, 4.45.

Decarboxylation of 3 to 8. Diacid 3 was heated at 200-210 °C until evolution of CO_2 ceased. The resulting dark oil was quickly distilled by connecting the reaction flask to the distillation device and water pump: Colorless distillate, bp 160-165 °C,[21] ^1H NMR ($CDCl_3$) δ 2.02 (s, 3 H), 2.09 (s, 3 H), 3.31 (s, 3 H), 5.05 (s, 1 H), 6.19 (s, 1 H). Compound 8 is very unstable and turns red when applied to a TLC plate. It can be stored cool under Ar or N_2.

Kinetic Measurements. Solutions of 2 (0.044 M and 0.022 M) were prepared in 84.6% phosphoric acid, and 100 mg (0.44 mmol) of 2 and 0.052 mL (0.88 mmol) of absolute ethanol were mixed with phosphoric acid in a 10-mL volumetric flask. One milliliter of the first two solutions was pipetted into each of 12 test tubes, and 1 mL of the last solution into 8. The tubes were placed in a thermostated water bath at 61 ± 0.1 °C. At 15-min intervals (25 min in the case of 2 and ethanol) the tubes were removed from the bath, and the mixture was diluted with 5 mL of water and extracted with 5 mL of a chloroform solution of 1 (1.9 mg/mL), which served as an internal standard for GC analysis. Then 0.2 mL of the chloroform extract was pipetted out and mixed with 0.1 mL of ethereal diazomethane solution. When evolution of nitrogen ceased, the yellow solution was injected into the gas chromatograph. Values for k_{obsd} were calculated by the least-squares method. Correlation factors were >0.99 for each run.

Acknowledgment. We are grateful to Dr. M. Biruš, Faculty of Pharmacy and Biochemistry, University of Zagreb, for his helpful discussions.

Registry No. 1, 33369-26-5; 2, 82875-55-6; 3, 33369-45-8; 4, 79673-54-4; 5, 33369-47-0; 6, 33369-46-9; 8, 931-25-9; 9, 33369-27-6; 10, 94324-21-7; 11, 94324-22-8.

(20) Sun, T. H.; Abbott, F. S.; Burton, R.; Orr, J. *J. Labeled Compd. Radiopharm.* **1982**, *19*, 1043.
(21) Triebs, A.; Dietl, A. *Liebigs Ann. Chem.* **1958**, *619*, 80.

Photooxygenation of (*R*)-*p*-Mentha-3,8(9)-diene and 1-Isopropenyl-3,4-dihydronaphthalenes. Preparation of (*R*)-Menthofuran, (*R*)-Evodone, and (±)-Chromolaenin[1]

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As part of our study of the competition between "ene" reaction and the 1,4-cycloaddition reaction of singlet oxygen in a series of 1-vinylcycloalkenes **1a** and **1b**,[2] we decided to reinvestigate the photooxygenation of (*R*)-*p*-mentha-3,8(9)-diene (**2**) and to examine the behavior of 1-isopropenyl-3,4-dihydronaphthalenes of type **3** (Chart I).

As regards **2**, its conversion into (*R*)-*p*-menthofuran (**4**) via endoperoxide **5** has been reported,[3] but this intermediate, the sole product mentioned, was not characterized and no yield was given. In analogy with the photooxygenation of **1b** (n = 6),[2] the optically active diene **2** would be expected to give, after $P(OEt)_3$ treatment, not only a mixture of 1,4-cycloaddition products **5a,b** but also minor ene products such as **6a,b** as well as some or all of the compounds (**7a,b**, **8a,b**, **9a,b**, and **10a,b**) resulting from further reactions of **5a,b** and **6a,b** with $^1O_2$. Moreover, as the C-1 methyl group of **2** is presumably pseudoequatorial,[4] it should have little effect on the relative rates of attack (cis or trans) by $^1O_2$, and the proportions of the initial product **5a,b** or **6a,b** could presumably furnish additional information on the direction of $^1O_2$ approach to the reaction site for 1-vinylcycloalkenes.

As regards compounds of type **3a,b**, the only ene reactions which these substances can undergo would lead either to **3c** or to tertiary allylic hydroperoxides **11** in which the double bond is deconjugated. Formation of such products is not in accord with previous experiments in the 1-vinylcyclohexene series,[2] although in 1,2-dihydronaphthalenes of type **12** the ene reaction can compete successfully with 1,4-cycloaddition to the styrene system, the latter leading to compounds of type **13** and their transformation products.[5,6] It was of interest to ascertain whether such reactions could compete with 1,4-cycloaddition to the semicyclic diene system of **3**.

Photooxygenation of 2. (*R*)-3-Menthenol was prepared from (*R*)-(+)-pulegone by the literature method[7] and converted to **2** in 42% yield by dehydration with $POCl_3$-pyridine. Photooxygenation of **2** under our standard conditions[2] gave a 1:1 mixture of the 1,2-dioxin epimers **5a,b**, a 5:4 mixture of the dienols **6a,b**, and a mixture of polar substances in 58%, 10%, and approximately 15% yields, respectively.

The NMR spectra of the two 1,2-dioxin epimers exhibited superimposed signals for H-3, H-3', and the C-4 methyl group, but the signals of H-8a and the C-7 methyl appeared at different fields, δ 4.74 (J = 11 Hz) and δ 1.09

(1) Supported in part by a grant from the U.S. Public Health Service (CA-13121) through the National Cancer Institute.
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(5) Burns, P. A.; Foote, C. S. *J. Org. Chem.* **1976**, *41*, 908.
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