thermolyzed at 160°. **2g** was precipitated from the reaction mixture by the addition of hexane; the compound (1.25 g) was collected by filtration. An additional 0.60 g was obtained by extraction of the filtrate with NaOH solution. The total crude yield was 62%. Crystallization from water gave a pure sample: mp 187°; ir 3175 (NH), 1525 and 1350 (1370?) cm^{-1} (CNO_2); nmr (60 MHz, $CDCl_3$) 7.80 [s, 1, 5(3)-H] and 2.47 (s, 3, CH_3).

Anal. Calcd for $C_4H_5N_3O_2$: C, 37.80; H, 3.97; N, 33.06. Found: C, 37.92; H, 4.07; N, 32.97.

3(5),4-Dinitro-5(3)-phenylpyrazole (2k). Rearrangement of 1k.—A 0.30-g portion of **1k** was dissolved in 5 ml of benzonitrile and thermolyzed at 140°; the resulting solution was worked up by extraction with NaOH solution. The crude yield was 0.24 g (80%). Crystallization from benzene gave an analytically pure sample: mp 149–150°; ir 3280 (NH), 1535 (m), 1370 and 1330 cm^{-1} (CNO_2); nmr (100 MHz, acetone) δ 7.9–7.7 (m, 2) and 7.7–7.5 (m, 3, aromatic).

Anal. Calcd for $C_9H_6N_4O_4$: C, 46.16; H, 2.58; N, 23.93. Found: 46.43; H, 2.72; N, 23.74.

Thermolysis of 1i.—A 2% solution of **1i** in benzonitrile was heated at 120°; the reaction was followed by tlc. Among other products, the rearrangement product 3(5)-nitro-4-phenylpyrazole (**2i**)[33] could be detected.

3(5),4-Dinitropyrazole (2j). Nitration of 2a with Mixed Acid.—Compound **2a** (1.5 g) was dissolved in 2.55 ml of concentrated sulfuric acid and nitrated by the method of Morgan and Ackerman[31] with 1.65 ml of nitric acid and 5.1 ml of sulfuric acid. The reaction mixture was poured on ice and, after saturation with NaCl, extracted with ether. Removal of the solvent gave 1.9 g (86%) of **2j** as white crystals from benzene: mp 87.5–88.5°; ir 3280 (NH), 1550, 1520, 1370, and 1340 cm^{-1} (NO_2); nmr (60 MHz, acetone) δ 8.71 [s, 5(3)-H]; mol wt, 158.0078 (calcd for $C_3H_2N_4O_4$, 158.0075).

Thermolysis of 1j.—The reaction mixture that was obtained when a solution of **1j** in benzonitrile (10%) was refluxed for 6 hr was worked up by extraction with NaOH solution. The oily liquid that was obtained appeared to be mainly a mixture of **2j** and **4a** (8:2, nmr analysis). When a solution of **1j** was heated for a longer time at a lower temperature (130°), other (unknown) products were formed.

3(5),4-Dinitro-5(3)-methylpyrazole (8).—Compound **2b** (0.80 g) was nitrated by the method of Morgan and Ackerman.[31] The reaction mixture was poured onto ice, neutralized with sodium carbonate, and extracted with ether, yield 0.78 g (72%). Crystallization from benzene gave an analytically pure sample: mp 120–121°; ir 3280 (NH), 1550, 1505, 1360, and 1330 cm^{-1} (NO_2); nmr (60 MHz, acetone) δ 2.67 (s, CH_3).

Anal. Calcd for $C_4H_4N_4O_4$: C, 27.91; H, 2.34; N, 32.56. Found: C, 28.33; H, 2.49; N, 32.30.

3,5-Dinitro-4-ethylpyrazole (7).—The reaction mixture that was obtained after nitration of 1.5 g of **2h** by the method of Morgan and Ackerman[31] was poured onto ice; the formed precipitate (unreacted **2h**) was removed by filtration; the filtrate was neutralized with sodium carbonate and extracted with ether to yield 0.48 g (23%) of **7**. The compound was purified by column chromatography[11] (silica gel H according to Stahl, chloroform–methanol–acetic acid, 80:20:0.5, as eluent) and crystallization from water: mp 170–171°; ir 3245 (NH), 1590 (?), 1545 and 1340 cm^{-1} (NO_2); nmr (100 MHz, hexadeuterioacetone) δ 3.19 (q, 2, CH_2) and 2.24 (t, 3, CH_3).

Anal. Calcd for $C_5H_6N_4O_4$: C, 32.26; H, 3.25; N, 30.10. Found: C, 32.71; H, 3.35; N, 30.26.

Nitration of 4-Nitropyrazole (4a).—This compound was treated with mixed acid by the same method that was used for the further nitration of **2a**. Work-up of the reaction mixture afforded the unreacted compound as the only product (tlc analysis).

Registry No.—**1a**, 7119-95-1; **1c**, 38859-25-5; **1d**, 38859-26-6; **1e**, 38859-27-7; **1f**, 38858-81-0; **1g**, 38858-82-1; **1j**, 35852-77-8; **1k**, 38858-84-3; **2a**, 26621-44-3; **2c**, 38858-86-5; **2d**, 38858-87-6; **2e**, 38858-88-7; **2f**, 38858-89-8; **2g**, 38858-90-1; **2h**, 31163-87-8; **2j**, 38858-92-3; **2k**, 38858-93-4; **4a**, 2075-46-9; **4c**, 38858-95-6; **4d**, 38858-96-7; **4e**, 38858-97-8; **6**, 38858-98-9; **7**, 38858-99-0; **8**, 38859-00-6; 3(5)-phenylpyrazole, 2458-26-6; 4-nitro-3(5)-(*p*-aminophenyl)pyrazole, 38859-02-8; 3(5)-methylpyrazole, 1453-58-3; 3(5)-(*p*-nitrophenyl)pyrazole, 20583-31-7; 4-methylpyrazole, 7554-65-6.

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(33) We wish to thank Dr. W. E. Parham, University of Minnesota, for providing a sample of this compound.

On the Reaction of Carbonyl Compounds with 3,5-Dihydroxy-4-phenylisoxazole. A Novel Type of Noncatalyzed Condensation and Carbon–Carbon Bond Formation

GURY ZVILICHOVSKY* AND UPINDER FOTADAR

Department of Organic Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

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3,5-Dihydroxy-4-phenylisoxazole reacts spontaneously with a variety of carbonyl compounds yielding with aromatic aldehydes *N*-arylmethylidene-4-phenylisoxazol-5-onium-3-enolates and with acetone a 1:2 condensation product. The latter undergoes reaction with alcohols giving 5-alkoxy-2-oxo-3-phenyl-5,7,7-trimethyl-2*H*,7*H*-isoxazolo[3,2-*b*][1,3]oxazine. Crotonaldehyde, acrolein, and mesityl oxide reacted with the initial isoxazole. Structures and properties of the various products are studied.

The unusual physical properties of 3,5-dihydroxy-4-phenylisoxazole (**1**), prepared from ethyl α-phenylmalonate and hydroxylamine, have been described recently.[1] An interesting chemical property of this compound which is studied here is its reactivity toward carbonyl compounds. It reacts spontaneously either upon dissolution in the neat carbonyl compound or in solution, at room temperature. The stable red products which are obtained from aromatic aldehydes were briefly described in a recent communication[2] and were proved to be *N*-arylmethylidene-4-phenylisoxazol-5-onium-3-enolates (**2**). Additional data about these compounds are given in the Experimental Section below. The formation of **2** is probably initiated by the protonation of the aldehydic oxygen by the very acidic[1] enol of **1**, followed by the elimination of water. Another possible approach is a cyclic concerted mechanism (see Scheme I). In the case of benzaldehyde the re-

(1) G. Zvilichovsky, *Israel J. Chem.*, **9**, 659 (1971).

(2) G. Zvilichovsky, *Tetrahedron Lett.*, 2351 (1972).

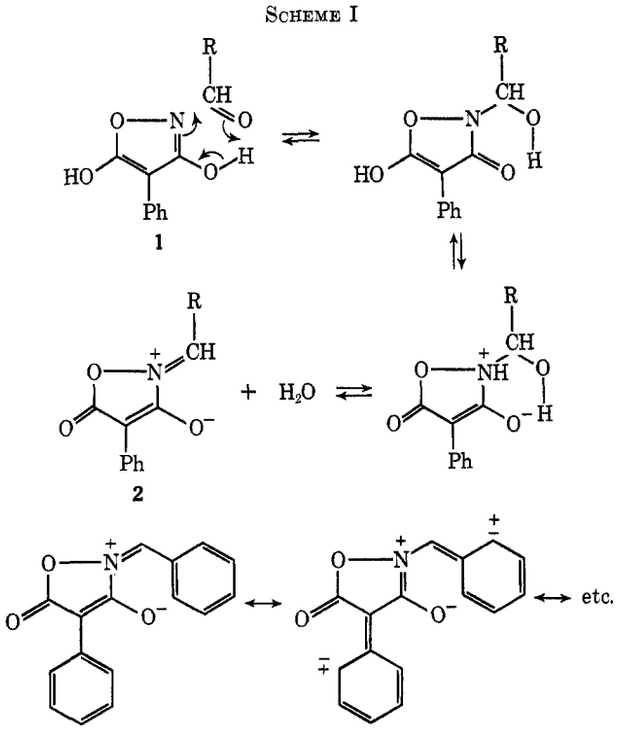
TABLE I

NMR DATA OF PRODUCTS DERIVED FROM ACETONE. δ VALUES AND RELATIVE INTEGRATION[a]

Compound no.	Solvent (time)[b]	CH_2	CH_3	$(CH_3)_2C$	OH
5	$CDCl_3$	2.92 s (1.6)	2.14 s (2.4)	1.54 s (4.8)	4.36 s (0.8)[c]
		2.36 s (0.4)	1.79 s (0.6)	1.40 s (1.2)	7.2 (0.2)
	Acetone-d_6	2.38 s (2.0)	1.79 s (3.0)	1.40 s (6.0)	7.2 (1.0)
	DMSO-d_6 (5 min)	2.55 s (2.0)	1.85 s (3.0)	1.38 s (6.0)	8.4 s (1.0)
	(10 min)[d]	2.55 s (1.9)	1.85 s (2.9)	1.38 s (5.7)	8.5 s (1.05)
			1.78 s (0.1)	1.87 d (0.3)[e]	
	(15 min)[d]	2.55 s (1.8)	1.85 s (2.7)	1.38 s (5.4)	8.9 s (1.1)
			1.78 s (0.3)	1.87 d (0.6)[e]	
	(25 min)[d]	2.55 s (1.6)	1.85 s (2.4)	1.38 s (4.8)	9.2 s (1.2)
			1.78 s (0.6)	1.87 d (1.2)[e]	9.2 s (1.2)
	(70 min)[d]	2.55 s (1.2)	1.85 s (1.8)	1.38 s (3.6)	9.6 s (1.4)
			1.78 s (1.2)	1.87 d (2.4)[e]	
	(20 hr)[d]	2.55 s (0.8)	1.85 s (1.2)	1.38 s (2.4)	10.0 s (1.6)
			1.78 s (1.8)	1.87 d (3.6)[e]	
	$CDCl_3$ + pyridine	2.92 s (2.0)	2.10 s (3.0)	1.48 s (6.0)	14.1 ($\overset{+}{N}H$)
	$CDCl_3$ + Et_3N	2.86 s (2.0)	2.05 s (3.0)	1.45 s (6.0)	10.2 ($\overset{+}{N}H$)
7, R = Et	$CDCl_3$	2.20 s (2.0)	1.60 s (3.0)	1.40 s (3.0)	1.0 t (OEt)
				1.34 s (3.0)	3.5 q (OEt)
7, R = Me	$CDCl_3$	2.22 s (2.0)	1.60 s (3.0)	1.40 s (3.0)	3.28 s (OMe)
				1.37 s (3.0)	

[a] The signals of the aromatic protons are not given in the table. In $CDCl_3$ **5** gave δ 7.20 s (4.0) and 7.20–7.60 m (1.0). In all other solvents a multiplet is observed. **7** gave a multiplet. [b] The time after the sample was dissolved. [c] This is the absorption of the methine proton of tautomer **5c**. [d] A vinylic proton signal is also observed: δ 5.98 with increasing integration from 0.05 to 0.6. [e] This doublet is actually two singlets.

SCHEME I



action is reversible, and by addition of water it decomposes to the parent compounds. These red crystalline products (**2**) are stabilized by conjugation of the aldehydic component with the phenyl group at the 4 position, with a large number of resonance structures as shown for the benzaldehyde derivative (**3**). The stability of these zwitterionic compounds depends on the nature of the aldehyde; extended conjugation or electron-donating groups enhance their stability.[2] In the case of acetone, acrolein, or crotonaldehyde there is a more limited electron delocalization. Thus the zwitterionic analog of **2** becomes an active intermediate with a strongly electrophilic carbon, comparable to the carbon in phosgene immonium[3-5] or in the intermediate cyclopropanone imminium salt.[6]

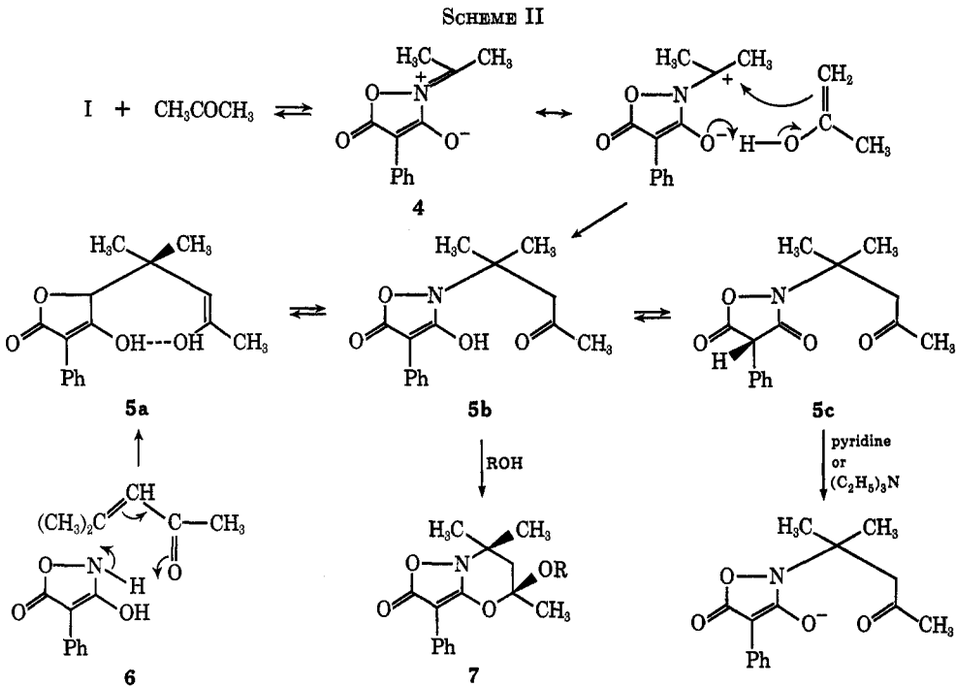
It was mentioned previously[1] that 3,5-dihydroxy-4-phenylisoxazole (**1**) gives a yellow coloration with acetone. Attempts to isolate the colored product were unsuccessful. However, a new colorless product could be obtained in about 50% yield (**5**). The product gave analytical results of a condensation product of two molecules of acetone per molecule of **1**, with the elimination of a molecule of water and has probably structure **5** (Scheme II). On hydrolysis it yields phenylacetic acid, excluding combination of any acetone molecule to any ring carbon, as phenylacetic acid is obtained *via* phenylmalonic acid by decarboxylation.

It appears that the strongly electrophilic carbon in **4** attacks the carbon of the ketone even in the absence of base. Evidence for the structure of **5** is also obtained from its spectral and chemical properties. The ir in the solid state shows a C=O absorption only at 1700 cm^{-1} which is probably due to the side-chain carbonyl group. The ring carbonyl absorption is absent similarly to the case of the parent compound as a result of tautomerism and hydrogen bonding.[1] The low frequency of the OH absorption (3210 cm^{-1}) also indicates hydrogen bonding in the solid state. The tautomeric equilibria of **5** are clearly seen in the nmr spectra (Table I).

The nmr absorption of the phenyl protons in the parent compound (**1**) consists of a multiplet rather than a singlet;[1] however, by determining the nmr spectrum of **5** in $CDCl_3$ a mixture of tautomers is observed. About 20% has a conjugated structure (**5b**), showing

(3) H. G. Viehe and Z. Janosek, *Angew. Chem., Int. Ed.* Engl., **10**, 573 (1971); *Angew. Chem.*, **83**, 614 (1971).
(4) Z. Janosek and H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **10**, 574 (1971); *Angew. Chem.*, **83**, 615 (1971).
(5) H. G. Viehe, Z. Janosek, and M.-A. DeFrenne, *Angew. Chem., Int. Ed. Engl.*, **10**, 575 (1971); *Angew. Chem.*, **83**, 616 (1971).
(6) H. H. Wasserman and M. S. Baird, *Tetrahedron Lett.*, 3721 (1971).

SCHEME II



the aromatic multiplet, whereas about 80% give a singlet at δ 7.10 corresponding to structure **5c**. In addition there is a methine band at δ 4.35 which also arises from structure **5c**; this band is displaceable by D_2O. The side-chain bands indicate CH_2, CH_3CO, and $(CH_3)_2C$ groups at δ 2.92, 2.14, and 1.54, respectively. These bands are accompanied by bands of 20% intensity at δ 2.36, 1.79, and 1.40, respectively. Moreover, if structure **5c** is dominant in $CDCl_3$, the absorption of the ring carbonyl in the ir should be observed at higher frequencies, and, indeed, there are two carbonyl bands in chloroform at considerably higher frequency (1810 and 1730–1700 cm^{-1}) resembling cyclic anhydrides. Upon the addition of an organic base to the $CDCl_3$ solution, *e.g.*, pyridine or triethylamine, 100% of the enolic form is obtained resulting in a complete elimination of the aromatic singlet and in single peaks for each kind of the aliphatic protons of the side chain (see Table I). The enolic form is also favorable in acetone-d_6 as observed in the nmr spectrum (Table I), probably because of hydrogen bonding with molecules of the solvent. In DMSO-d_6 the conjugated enolic form exists; furthermore, it causes also enolization of the side-chain carbonyl. This enolization is slow and can be followed by changes in the nmr; it reaches a maximum of about 60% after 20 hr. In moist DMSO-d_6 the change is faster and there is also a shift upfield in the band of the acidic proton. Similar to what is observed in the semihydrate of the parent compound (**1**),[1] both the ring OH protons and the external OH protons give a single peak. During the enolization process this peak moves from δ 8.5 to 10.0 (in wet DMSO-d_6 it moves rather upfield). This enolization of the side chain is indicated by the decrease in the CH_2 protons band at δ 2.55 and the formation of a vinylic proton which absorbs at δ 5.98. The terminal methyl protons signal moves about 4 Hz upfield and the two geminal methyl groups become nonequivalent yielding two bands at δ 2.00 and 1.98 instead of one peak at δ 1.35. This is probably due to hydrogen bonding as shown in structure **5a**. Precipitation of **5a** from its DMSO solution and redissolution in $CDCl_3$ restores tautomer **5c**. This fact excludes any irreversible changes in DMSO and indicates proton tautomerization.

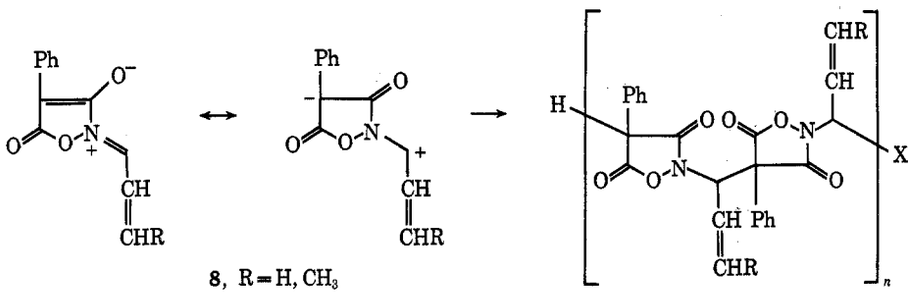
On a short heating of **5** in alcohols, *e.g.*, ethanol or methanol, a new heterocyclic compound was obtained. An attack of the alcoholic oxygen on the side-chain carbonyl is followed by a ring closure to a derivative of the unknown isoxazolo[3,2-*b*][1,3]oxazine bicyclic system (**7**). The nmr spectrum of **7** shows, as expected, a multiplet of the phenyl protons, indicating the conjugation of the phenyl group with the isoxazolone ring. The two geminal methyl protons are not equivalent in **7**, as they occur on either side of the plane of the ring system and as a result their signals are separated by 4 Hz in the ethoxy derivative (R = C_2H_5) at δ 1.33 and 1.38, respectively, and by a smaller difference in the methoxy derivative (R = CH_3).

A final proof for the structure of **5** was provided by the formation of an identical product by the reaction of **1** with mesityl oxide. The latter reaction represents another possible reaction of 3,5-dihydroxy-4-phenylisoxazole (**1**) with a carbonyl compound, *e.g.*, a noncatalyzed Michael addition (formulation **6**, Scheme II).

On the basis of the above findings it was easier to understand the reaction of 3,5-dihydroxy-4-phenylisoxazole (**1**) with crotonaldehyde or acrolein. Here again the stabilization of the immonium enolate species is too small and the aldehydic carbon becomes strongly electrophilic. By introducing crotonaldehyde to the solution of **1** in dry ether the red color which is formed initially disappears while a colorless precipitate deposits. This product was shown to have a polymeric structure **9** (Scheme III).

In the absence of an external active α carbon the electrophilic carbon attacks the nucleophilic carbon in intermediate **8**. The polymer contains successive saturated isoxazole-3,5-dione rings. This fact is well observed in the ir spectra where we find two carbonyl bands, one at as high frequency as 1825 cm^{-1} and a

SCHEME III



8, R = H, CH_3

9

second at 1730 cm^{-1} (see Table II), indicating the omission of tautomerism which results in a cyclic anhydride-like structure. The phenyl protons give a singlet in the nmr as expected from the nonconjugated structure of the polymer (**9**). The nmr spectra has a kind of a diffused feature. This arises not only from the polymeric nature of the compound but also from the presence of free radicals. It is difficult to explain the presence of two superimposed peaks at about $g = 2$ in the esr spectrum of **9**. One explanation is the resemblance of the carbon in the 4 position to that in certain malonic acid derivatives that undergo easy heterolytic fission.[7]

TABLE II

CARBONYL AND HYDROXYL ABSORPTION (cm^{-1})

Compd	Phase	CO	OH
1	Nujol	1680 weak	2500–2580
3	Nujol	1780, 1700	
5	Nujol	1700	3220
	$CHCl_3$	1810, 1700–1730	
	DMSO	1730	
7	Nujol	1735	
9	Nujol	1825, 1730	

Dimers (**9**, $n = 2$) could be obtained by carrying out the reaction in alcohols (X = OR) or in wet solvents (X = OH). Acrolein reacts with **1** similarly to crotonaldehyde.

Upon treatment of **1** with citral a very stable red product is obtained. This product could be obtained in a pure crystalline form, but contrary to its analogs of the aromatic series (**2**) it is soluble in aprotic nonpolar solvents. This was the only case in which it was possible to determine the nmr spectrum of a red isoxazolium enolate derivative. Citral consists of two isomers geranial and neral. The signals of the $^+N{=}CH$ protons of the two geometric isomers are at δ 8.15 and 8.20, respectively, and are coupled with the vinylic protons (J = 10 Hz). The aromatic protons of the phenyl group are split into two multiplets.

The above variety of unusual reactions of 3,5-dihydroxy-4-phenylisoxazole with carbonyl compounds and their synthetical applications are being investigated further. It seems that the unique chemical reactivity arises from the participation of the strongly acidic enol and can be classified as neighboring group effect in a nucleophilic reaction. The remarkably ready carbon–carbon bond formation is a result of the combination with the strong electron attraction of the isoxazolone system which is responsible for its unusual physical properties as well.

(7) H. A. P. de Jongh, C. R. H. I. de Jonge, H. J. M. Sinnige, W. J. de Klein, W. G. B. Huysmans, and W. J. Mijs, *J. Org. Chem.*, **37**, 1960 (1972).

Experimental Section

Melting points are uncorrected. Nmr spectra were determined with a Varian T-60 spectrometer. Visible and uv spectra with a Unicam SP 800A recording spectrophotometer.

Reaction of 3,5-Dihydroxy-4-phenylisoxazole with Acetone.—3,5-dihydroxy-4-phenylisoxazole (**1**) which was previously dried on P_2O_5 at 100° *in vacuo* (10 g) was dissolved with mild heating in acetone (15 ml) and kept at room temperature. After 12 hr an additional 15 ml of acetone was added and the precipitate was suspended in the reaction mixture. This was kept overnight at room temperature. The crystals were collected and recrystallized by dissolving in chloroform, filtering, and reprecipitating with petroleum ether (bp 40–60). The pure crystals of **5** are colorless (7.6 g, 48% yield), mp 138°.

Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09; mol wt 275.3. Found: C, 65.56; H, 6.13; N, 5.03; mol wt 275 (mass spectrum).

5-Alkoxy-2-oxo-3-phenyl-5,7,7-trimethyl-2*H*,7*H*-isoxazolo-[3,2-*b*][1,3]oxazine (**7**).—The diacetone derivative (**5**) (1 g) was heated to boiling in alcohol (20 ml). The clear solution which resulted was concentrated *in vacuo* to a small volume. Beautiful colorless crystals precipitated on cooling. The product (**7**) could be recrystallized from a small amount of alcohol.

Both in ethanol and methanol the yield was ~1 g (90–95%).

The 5-ethoxy derivative (**7**, R = C_2H_5) melted at 123°.

Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.31; H, 6.98; N, 4.62; mol wt 303.4. Found: C, 67.38; H, 6.80; N, 4.57; mol wt 303 (mass spectrum).

The 5-methoxy derivative (**7**, R = CH_3) melted at 135°.

Anal. Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84; mol wt 289.3. Found: C, 66.30; H, 6.80; N, 4.81; mol wt 289 (mass spectrom.).

The Reaction of 3,5-Dihydroxy-4-phenylisoxazole (**1**) **with Crotonaldehyde.**—Anhydrous 3,5-dihydroxyisoxazole (**1**) (5 g) was dissolved in dry ether (100 ml) and crotonaldehyde (1.8 ml) was added while shaking and cooling on ice. The red color which was initially formed disappeared and a colorless precipitate was formed. The polymer (**9**) was recrystallized from chloroform–petroleum ether (bp 40–60). It melted with decomposition at 230–240° (3.5 g, 54%).

Anal. Calcd for $(C_{11}H_{11}NO_3)_n$: C, 68.11; H, 4.84; N, 6.11. Found: C, 67.63; H, 4.43; N, 6.28.

On carrying the reaction in ethanol instead of ether a dimeric product was obtained (**9**, n = 1, X = OC_2H_5). It turns brownish at 150° and decomposes at 230° (4.5 g, 70%).

Anal. Calcd for $C_{28}H_{28}N_2O_7$: C, 66.66; H, 5.59; N, 5.55; C_2H_5O, 8.92. Found: C, 66.35; H, 5.45; N, 5.62; C_2H_5O, 8.89.

In methanol, a similar compound was obtained in about the same yield.

Anal. Calcd for $C_{27}H_{26}N_2O_7$: C, 66.11; H, 5.34; N, 5.71. Found: C, 66.33; H, 5.20; N, 5.56.

An analogous compound but in a lower yield was obtained in butanol.

Anal. Calcd for $C_{30}H_{32}N_2O_7$: C, 67.66; H, 6.06; N, 5.26. Found: C, 68.37; H, 6.12; N, 5.01.

The Reaction of 3,5-Dihydroxy-4-phenylisoxazole (**1**) **with Acrolein.**—Anhydrous **1** was treated as above with acrolein instead of crotonaldehyde. In this case the red coloration of the

TABLE III

N-ALKYLIDENE- AND *N*-ARYLMETHYLIDENE-4-PHENYLISOXAZOL-5-ONIUM-3-ENOLATES (2)[a]

R	Registry no.	Method	Mp, °C (dec)	Yield, %	Visabsorption, λ_{max}, nm (ϵ),[b] in dioxane
C_6H_5	37118-32-4	B	215	45	480 (4,000)
CH=CHCH=C (—O—)	38896-39-8	A	198	55	484 (4,300)
$C_6H_5CH=CH$	37125-34-1	A	235	95	525 (5,000)
$2,3\text{-}(OMe)_2C_6H_3$	38896-41-2	A	220	60	468 (4,000)
$2,4\text{-}(OMe)_2C_6H_3$	38896-42-3	A	221	70	466 (4,300)
$3,4\text{-}(OMe)_2C_6H_3$	38896-43-4	A	216	45	468 (2,000)
$2\text{-}OHC_6H_4$	38896-44-5	B	204–205	35	475 (1,000)
$3\text{-}OMe\text{-}4\text{-}OHC_6H_3$	38896-45-6	B	208	40	460 (2,000)
$4\text{-}OMeC_6H_4$	38896-46-7	C[c]	218	85	466 (4,000)
$(CH_3)_2C=CH(CH_2)_2\text{-}C(CH_3)=CH$	38896-47-8	C	104	80	485 (4,000)[d]
$4\text{-}NMe_2C_6H_4$	37118-33-5	A C[c]	233	100	408 (25,000)

[a] Satisfactory analytical data (±0.3% for C, H, N) were reported for all compounds in table. [b] The visible spectra were taken in dry dioxane; the values of the molar extinction coefficient are approximate because of the instability of these solutions, except the 4-dimethylaminobenzylidene derivative which is very slightly soluble in dioxane but the solution is stable in the dark. [c] Requires protection against daylight during preparation and storing. [d] This compound is considerably soluble in organic aprotic solvents like dioxane, tetrahydrofuran, or chloroform and gives quite stable solutions.

solution could not be observed, but the results were similar. The polymeric product was obtained in a low yield (15%), but the dimeric products were obtained in good yields (70–80%). Analytical results were satisfactory. Spectral properties were also similar to the crotonaldehyde products. A similar signal in the esr spectrum could be observed at $g \simeq 2$.

The Reaction of 3,5-Dihydroxy-4-phenylisoxazole (1) with Mesityl Oxide.—3,5-Dihydroxy-4-phenylisoxazole (1) (1.77 g) was dissolved by heating for 5 min in boiling mesityl oxide (8 ml). Alternatively 1 was dissolved in THF (4 ml) and after the addition of mesityl oxide (5 ml) the solution was boiled for 3 min. In both ways the reaction mixture was cooled in the freezer overnight, and the precipitate which deposited was collected and recrystallized from chloroform–petroleum ether (bp 40–60). The product melted at 140–142° (2 g, 87% yield). Ir, nmr, and elementary analysis were identical with the product which was obtained from 1 with acetone (see above). This product could be also converted into the isoxazolo[3,2-*b*][1,3]oxazine derivative 7.

***N*-Alkylidene- and *N*-Arylmethylidene-4-phenylisoxazol-5-onium-3-enolates (2). Method A.**—3,5-Dihydroxy-4-phenylisoxazole (1) semihydrate (1.86 g, 0.01 mol) was dissolved in tetrahydrofuran (30 ml) and the aldehyde (0.01 mol) added in tetrahydrofuran (15 ml). The solution was shaken for a few seconds and kept overnight at 4°. The crystals which separated were collected and dried over P_2O_5 at 100°. In the case of 4-dimethylaminobenzaldehyde the reaction was carried out in the dark and the product was dried and kept in the dark. The results are summarized in Table III.

Method B.—3,5-Dihydroxy-4-phenylisoxazole (1) semihydrate (1.86 g, 0.01 mol) was dissolved in tetrahydrofuran (30 ml) and the aldehyde (0.01 mol) was added in ether (15 ml). The red solution was shaken for a few seconds and petroleum ether (bp 40–60) or *n*-hexane (15 ml) was added. Upon keeping at 4° the red crystals separated. They were collected and treated as above. The results are summarized in Table III.

Method C.—3,5-Dihydroxy-4-phenylisoxazole (1) semihydrate (1.86 g, 0.01 mol) is dissolved in absolute ethanol (30 ml) and the aldehyde (0.01 mol) is added in absolute ethanol (30 ml). After being shaken for a few seconds the red crystals are allowed to settle for a few minutes and collected by filtration. Decomposition of the product occurs if the solution is kept too long. In the case of anisaldehyde and *p*-dimethylaminobenzaldehyde protection against daylight is essential during preparation and storing of the red product. The results are summarized in Table III.

Decomposition of *N*-Benzylidene-4-phenylisoxazol-5-onium-3-enolate by Water.—*N*-Benzylidene-4-phenylisoxazol-5-onium-3-enolate (3) (0.53 g) was stirred in tetrahydrofuran (5 ml) at 40° while water was added portionwise until the red solution turned almost colorless (about 0.4 ml of water). Chloroform (35 ml) was added and the mixture was cooled on ice for 3 hr. The white crystals (0.32 g) which separated were found identical by mp and ir with 3,5-dihydroxy-4-phenylisoxazole (1). The filtrate was concentrated *in vacuo* to 10 ml; a solution of 2,4-dinitrophenylhydrazine (0.5 g) in ethanol (25 ml), containing some drops of concentrated hydrochloric acid, was added; and the solution was cooled again for a few hours. 2,4-Dinitrophenylhydrazone of benzaldehyde (0.15 g) precipitated and was identified by mp and ir spectrum. A better yield of the 2,4-dinitrophenylhydrazone (0.3 g) could be obtained by adding the 2,4-dinitrophenylhydrazine to the decomposition mixture, before adding the chloroform, without isolation of (1).

TABLE IV

NMR DATA OF THE REDUCTION PRODUCT OF 2 WITH ZINC IN ACETIC ACID ($C_6H_5CH_2CONHCH_2Ar$)

Registry no.	Ar	Solvent	δ(C_6H_5)	δ(CH_2CO)	δ(NH)	δ(CH_2N)	δ(CH_3)
37125-35-2	$p\text{-}NMe_2C_6H_4$	$CDCl_3$	7.22 s (5)	3.43 s (2)	5.5 dif. (1)	4.20 d (2)	2.81 s (6)
		Acetone-d_6	7.26 s (5)	3.50 s (2)	dif.	4.20 d (2)	2.80 s (6)
		Acetone + D_2O	7.17 s (5)	3.41 s (2)		4.08 s (2)	2.70 s (6)
38896-50-3	$2,3\text{-}(OMe)_2C_6H_3$	$CDCl_3$	7.05 s (5)	3.43 s (2)	5.6 dif. (1)	4.20 d (2)	3.65 s (3), 3.56 s (3)
38896-51-4	$2,4\text{-}(OMe)_2C_6H_3$	Acetone-d_6	7.16 s (5)	3.43 s (2)	2.8 dif.	4.20 d (2)	3.65 s (6)

Reduction of *N*-(*p*-Dimethylaminobenzylidene)-4-phenylisoxazol-5-onium-3-enolate with Zinc Powder in Acetic Acid.—*N*-(*p*-Dimethylaminobenzylidene)-4-phenylisoxazol-5-onium-3-enolate (2, R = $p\text{-}NMe_2C_6H_4$) (2.0 g) was stirred in boiling acetic acid (70 ml) and zinc powder (4.5 g) was added portionwise until the solution became colorless (25 min). The solution was cooled to room temperature and filtered, and a solution of 5% sodium bicarbonate (500 ml) was added slowly while being cooled on ice. The solution was shaken vigorously to expel excess CO_2 and kept 24 hr at 4°. The solid which precipitated (1.6 g, 90%) was recrystallized twice from ethanol, mp 142°.

Anal. Calcd for $C_{17}H_{20}N_2O$: C, 76.09; H, 7.57; N, 10.44. Found: C, 76.04; H, 7.80; N, 10.57.

Nmr data of this compound are summarized in Table IV.

Other derivatives of 2 are unstable in boiling acetic acid and therefore could not be reduced in the same way. Only in the cases of 2,3- and 2,4-dimethoxybenzylidene derivatives could poor yield of the same type of reduction product be obtained. They were not completely pure but their spectral properties were in agreement with their postulated structure (Table IV).

Registry No.—**1**, 36190-14-4; **5**, 38896-53-6; **7** (R = Et), 38896-54-7; **7** (R = Me), 38896-55-8; **9**, 38882-67-6; **9** (*n* = 1, X = OEt), 38896-56-9; **9** (*n* = 1, X = OMe), 38896-57-0; **9** (*n* = 1, X = OBu), 38896-58-1; acetone, 67-64-1; crotonaldehyde, 4170-30-3; mesityl oxide, 141-79-7.