but not for Thy$^{\alpha}$Cl. Also, the synthesis goes more readily and provides somewhat better yields when Thy$^{\alpha}$Cl is used as the reactant. However, whether these reactions proceed in a stepwise manner as shown has not yet been studied.

Our structural assignment of Thy$^{\alpha}$OOH is corroborated by the spectral data. The ir spectrum shows bands of νO–O (875 cm^{-1}) and νCH$_2$–O (973, 1033, and 1071 cm^{-1}). The last two bands also appear in the ir spectrum of CH$_2$OH-containing analogue, Thy$^{\alpha}$OH, but are in greatly reduced intensities. This reduction is to be expected[8,9] for C–OOH as compared to analogous C–OH compounds. In the NMR spectrum, the assignments are rather straightforward; however, the signal for OOH is absent. Similarly, the signal for OH in Thy$^{\alpha}$OH is also absent. On the other hand, we observed[9] the OOH signal as a sharp singlet in a similar compound, 6-TOOH. When Thy$^{\alpha}$OOH was allowed to stand in (CD$_3$)$_2$SO, it was reduced to the corresponding alcohol, Thy$^{\alpha}$OH [NMR in (CD$_3$)$_2$SO: δ 4.17 (s, 2, CH$_2$), 7.32 (d, 1, J = 6 Hz, C$_6$H)]. However, in spite of its allylic hydroperoxide function, Thy$^{\alpha}$OOH is surprisingly stable in Me$_2$SO with an apparent half-life of approximately 14 days, whereas, 6-TOOH has an apparent half-life of 27 min at 35°C. No appreciable change can be detected when Thy$^{\alpha}$OOH is stored for 1 week at room temperature; however, in solution it is gradually converted to 5-formyluracil (5CHO-Ura). Because Thy$^{\alpha}$OOH and 5CHO-Ura are reactive species, they may interact with biomolecules and thus affect biological systems when they are formed directly or indirectly by radiation.

Furthermore, when Thy$^{\alpha}$OOH (0.1 mM) was irradiated with 254-nm light, it was quantitatively converted to 5CHO-Ura within 220 sec at a light intensity of 198 ergs/mm^2 sec^{-1} (without filter) with ϕ = 0.47 (when Corning filter No. 954 is used, ϕ = 0.27). This efficacious photoconversion may have relevance in the study of radiobiology. In addition, 5CHO-Ura has been identified as a photoproduct of Thy.[4]

Thy$^{\alpha}$OOH can be easily reduced to Thy in H$_2$O by hydrogenation in the presence of 10% Pd/C at room temperature.

In short, the characteristics of Thy$^{\alpha}$OOH make it an interesting compound to be considered in the study of radiation effects of biological systems.

Experimental Section

Preparation of 5-Hydroperoxymethyluracil (Thy$^{\alpha}$OOH). From 5-Methoxymethyluracil (Thy$^{\alpha}$OCH$_3$). The starting material was prepared according to the method of Santi and Pogolotti.[10] First, Thy$^{\alpha}$OCH$_3$ (62 mg, 40 mmol) was dissolved in 10 ml of 15% H$_2$O$_2$, then, dropwise, 50 μl of concentrated HCl in 5 ml of H$_2$O$_2$ was added. After standing at room temperature for 24 hr with stirring, the reaction solution was lyophilized. The residue was washed three times with cold water and the purified product (56 mg, 89%) was obtained by recrystallization from 10% methanol solution.

From 5-Hydroxymethyluracil (Thy$^{\alpha}$OH). The procedure is analogous to that described above. In this case, 57 mg (40 mmol) of Thy$^{\alpha}$OH was used and 57 mg (90%) of the purified Thy$^{\alpha}$OOH was obtained.

From 5-Chloromethyluracil (Thy$^{\alpha}$Cl). The starting material was synthesized according to the method of Giner-Sorolla and Medrek.[11] Thy$^{\alpha}$Cl (50 mg, 32 mmol) was added portionwise to 1 ml of 50% H$_2$O$_2$ solution with stirring. The product began to appear as fine crystals at the completion of the addition; however, the stirring was continued for an additional 30 min at room temperature. The product was collected by filtration and washed with 50% methanol until the washings gave a negative AgNO$_3$ test for Cl$^-$. Again, recrystallization was carried out in 10% MeOH solution and 45 mg (92%) of the purified product was obtained: mp >230° dec; λ_{max} (H$_2$O) 261 nm (ϵ 7500); ir (KBr film) 11.43 μ for –O–O–, 10.28, 9.68, and 9.34 μ for C–OOH, respectively; NMR [(CD$_3$)$_2$SO] δ 4.52 (s, 2, CH$_2$), 7.52 (d, 1, J = 6 Hz, C$_6$H), 9.47 (d, 1, J = 6 Hz, N$_1$H), and 9.67 (b, 1, N$_3$H); mass spectrum m/e 142 (M − 16). Anal. Calcd for C$_5$H$_6$N$_2$O$_4$: C, 38.00; H, 3.80; N, 17.71. Found: C, 37.88; H, 3.76; N, 17.79.

Reduction of Thy$^{\alpha}$OOH to Thy. Thy$^{\alpha}$OOH (31.7 mg, 20 mmol) and 10 mg of 10% Pd/C were suspended in 10 ml of water. The solution was shaken with H$_2$ at room temperature. A theoretical amount (9.6 ml, 2 molar equiv) of H$_2$ was taken up at the end of 4 hr. The catalyst was removed by filtration and the filtrate was evaporated until dry. The residue, after recrystallization from 20% methanol, gave 23.4 mg of thymine (~93% yield).

Formation of 5CHO-Ura from Thy$^{\alpha}$OOH by Irradiation (254 nm). Thy$^{\alpha}$OOH (5 mg, 36 μmol) was dissolved in 40 ml of water. The solution in a quartz tube was irradiated (254 nm) for 220 sec and evaporated until dry. The residue, after recrystallization from absolute methanol, gave 4.0 mg of 5CHO-Ura (88% yield), mp >300° dec, λ_{max} (H$_2$O) 278 nm (ϵ 11850).[12]

Acknowledgment. The authors wish to express appreciation to ERDA (Contract E(11-1)-3286) and to NIH (Contract RO1-GM21146) for financial support. (This publication is identified as No. COO-3286-13.) Appreciation is also expressed to Dr. Catherine Fenselau and Mrs. Nancy Kan for the mass spectral determinations.

Registry No.—Thy$^{\alpha}$OOH, 33499-50-2; Thy$^{\alpha}$OCH$_3$, 57346-43-7; Thy$^{\alpha}$OH, 4433-40-3; Thy$^{\alpha}$Cl, 3590-48-5; 5CHO-Ura, 1195-08-0.

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(5) *cis*-ho^{5}ho$_2$^{6}hThy is the abbreviation for this compound according to the system proposed in ref 2. However, TOOH has been used for various hydroperoxy thymine derivatives. Because we are dealing with ho^{5}ho$_2$^{6}hThy, ho$_2$^{5}ho^{6}hThy, and Thy$^{\alpha}$OOH at present, we propose that 6-TOOH, 5-TOOH, and α-TOOH, respectively, be used for brevity and distinction.
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Allylic Rearrangement from O^6 to N-3 and N-7 of Guanine Blocked at C-8

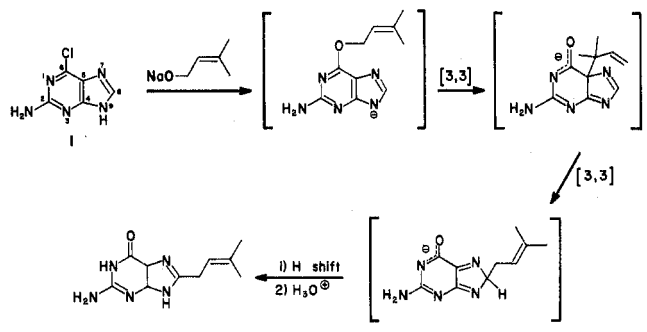
Brian N. Holmes[1] and Nelson J. Leonard*

Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

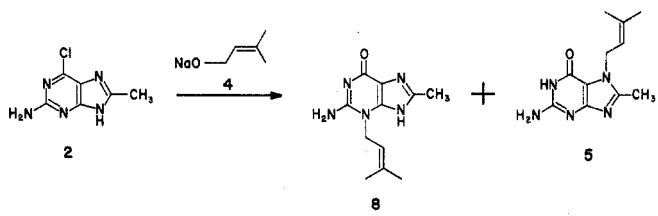
Received September 25, 1975

It was recently reported[2,3] from this laboratory that the displacement reaction of 2-amino-6-chloropurine (1) with the sodium salts of allylic alcohols proceeds through an O^6 ether to yield an 8-substituted guanine. The O^6 to C-8 rearrangement occurs intramolecularly and is judged to proceed by two anionic [3,3] sigmatropic shifts via C-5 (Scheme I). By blocking the 8 position of the purine ring with a methyl group, we sought to trap the C-5 intermediate or to redirect the migrating group. Thereby, another allylic rearrangement has been revealed in which the overall migration, with allylic retention, is from O^6 to the N-3 and N-7 positions of the guanine ring (Scheme II), with corresponding mechanistic implications.

Scheme I

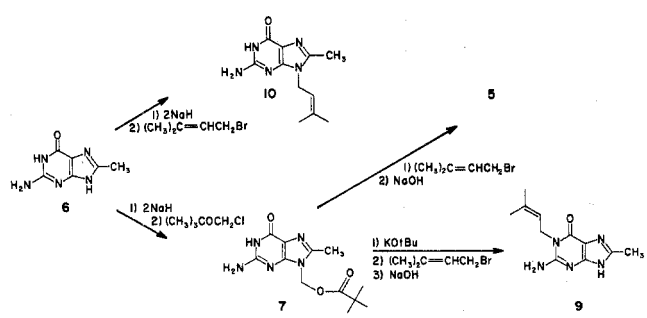


Scheme II



When 2-amino-6-chloro-8-methylpurine (**2**), prepared by reaction of 2-amino-6-mercapto-8-methylpurine (**3**)[4] with chlorine gas,[5] was allowed to react with sodium 3-methyl-2-butene 1-oxide (**4**) in refluxing dioxane (101°), a mixture of two *N*-isopentenyl-8-methylguanine products (2:1) was obtained in a total yield of 88%. After a separation by high-pressure liquid chromatography, the minor isomer was identified as 8-methyl-7-(3-methyl-2-butenyl)guanine (**5**) by comparison with an authentic sample prepared by independent synthesis. During consideration of possible synthetic routes to **5** we noted that 7-alkylguanine derivatives have, in general, been formed by alkylation of guanosine followed by hydrolytic removal of the ribose.[6] Since 8-methylguanosine is not readily available, a protecting group was sought that could be placed on N-9 of 8-methylguanine (**6**) and removed after alkylation at N-7. The pivaloyloxymethyl (POM) protecting group, employed for a similar purpose in the adenine series in the synthesis of cordycepin, for example,[7] was found satisfactory for the synthesis of **5**. Treatment of the disodium dianion of **6** with chloromethyl pivalate in dimethyl sulfoxide gave 8-methyl-9-pivaloyloxymethylguanine (**7**) in 92% yield. This compound was converted to isomer **5** by treatment with 3-methyl-2-butenyl bromide in dimethylformamide followed, without isolation, by basic hydrolysis of the POM protecting group in an overall yield of 55% (Scheme III). The

Scheme III

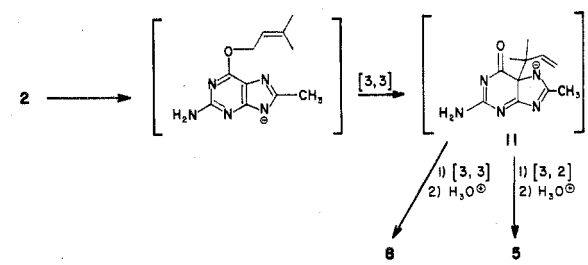


NMR, ultraviolet, and mass spectra of **5** prepared in this manner are identical with those of the minor isomer in the rearrangement mixture.

Although the ultraviolet spectrum strongly suggested that the major isomer was 8-methyl-3-(3-methyl-2-butenyl)guanine (**8**),[8] additional proof was obtained by synthesis of the remaining possible isomers, 8-methyl-1-(3-methyl-2-butenyl)guanine (**9**) and 8-methyl-9-(3-methyl-2-butenyl)guanine (**10**). Treatment of **7** with potassium *tert*-butoxide and 3-methyl-2-butenyl bromide followed by hydrolysis of the POM protecting group gave **9** in 13% yield. Derivative **10** was prepared in 36% yield by alkylation of the disodium dianion of **6** in dimethyl sulfoxide. The NMR and ultraviolet spectra for **9** and **10** do not correspond to those of the major rearrangement isomer, thus eliminating all but the N-3 isomer from consideration.

A mechanistic sequence for the formation of **8** and **5** can be formulated in terms of a C-5 bridgehead intermediate. Initial displacement on **2** followed by one [3,3] sigmatropic shift would yield the anionic bridgehead intermediate **11**. The major isomer **8** would then arise from a [3,3] sigmatropic rearrangement to N-3 (Scheme IV). The minor isomer **5**

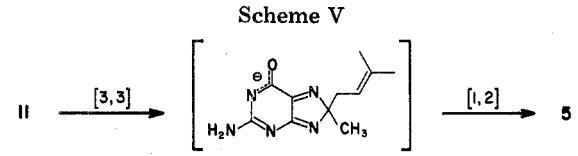
Scheme IV



could then arise by two possible routes. First, it might be formed directly by a [3,2] sigmatropic shift in the anion. Although it seems likely from steric considerations that the allylic migration to C-8 could occur to give a C-8 disubstituted derivative, the lack of a hydrogen for removal from C-8 as in Scheme I would favor reversal of the C-5 to C-8 rearrangement in the 8-methyl case. That the N-9 isomer (**10**) was not formed in the rearrangement is explicable on the basis of scale molecular models which show that the reactive end of the allylic moiety in the intermediate **11** is 15–20% further from N-9 than from either N-3 or N-7.

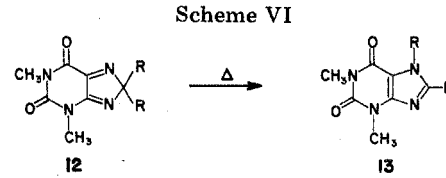
A second possible sequence is represented in Scheme V, in which a [3,3] sigmatropic shift from C-5 to C-8 would

Scheme V



produce a C-8 disubstituted intermediate that could then undergo a 1,2 migration to give **5**. The closest parallel is the thermal rearrangement of 1,3,8,8-tetrasubstituted pseudoxanthines (**12**) to 1,3,7,8-tetrasubstituted xanthines (**13**) exclusively.[9] The absence of any N-9 can be attributed to the energy barrier provided by the development of 3-8 peridialkyl interaction. In our system no such interaction would develop, and accordingly some N-9 isomer (**10**) would be expected. Since we were unable to detect the presence of any isomer **10** in the product resulting from the reaction of **2** and **4**, the [3,2] sigmatropic shift (Scheme IV) is favored for the conversion of the postulated intermediate **11** to 8-methyl-7-(3-methyl-2-butenyl)guanine (**5**).

Scheme VI



Experimental Section

All melting points are uncorrected. The NMR spectra were recorded on Varian Associates A-60 or HA-100 spectrometers using tetramethylsilane as an internal standard. The ultraviolet spectra were obtained on a Beckman Acta Model MVI spectrometer. Microanalyses were performed by Mr. Josef Nemeth and associates, who also weighed samples for quantitative electronic absorption spectra. Low-resolution mass spectra were obtained on a Varian MAT CH-5 spectrometer and high resolution on a Varian-MAT 731 spectrometer, both coupled with a 620i computer and STATOS recorder.

2-Amino-6-chloro-8-methylpurine (2). Chlorine gas was introduced at a slow rate into a stirred suspension of 2-amino-6-mercapto-8-methylpurine[4] (6 g, 33 mmol) and acetonitrile (100 ml) for 1.5 hr at room temperature.[5] After purging the system with nitrogen for 1 hr, the bright yellow hydrochloride salt was filtered and washed with cold acetonitrile (150 ml).

The free base was obtained by suspending the hydrochloride salt in 100 ml of water and adjusting the pH to 6.5. The water was then removed in vacuo and the residue was extracted with chloroform for 6 hr in a Soxhlet extractor. The chloroform was removed in vacuo, and the residue was recrystallized from methanol: yield 4.25 g (70%); mp 205–215° dec; λ_{max} (H_2O) 308 nm (ϵ 8070), 241.5 (6540), 217 (30200); (H_2O, 0.1 *N* HCl) 314 (8340), 237 (7960); (H_2O, 0.1 *N* NaOH) 302.5 (7740), 268 (3680); NMR (TFA) δ 3.00 (s, pu-CH_3); mass spectrum (10 eV) *m/e* 183 (M^+), 148 $(M - Cl)^+$.

Anal. Calcd for $C_6H_6ClN_5$: C, 39.25; H, 3.29; N, 38.15. Found: C, 39.14; H, 3.24; N, 38.12.

8-Methyl-3-(3-methyl-2-butenyl)guanine (8) and 8-Methyl-7-(3-methyl-2-butenyl)guanine (5). To a suspension of sodium hydride (0.5 g of a 51% oil dispersion, 12 mmol) in dry dioxane (40 ml), 3-methyl-2-buten-1-ol (1.00 g, 12 mmol) in dry dioxane (40 ml) was added under a nitrogen atmosphere. After evolution of hydrogen had ceased, 2-amino-6-chloro-8-methylpurine (**2**, 1.00 g, 5.9 mmol) was added and the mixture was heated at reflux for 20 hr. After cooling, the solvent was removed in vacuo, and the residue was dissolved in water (20 ml) and extracted five times with ether (50 ml). The aqueous layer was then acidified to pH 6 with 20% aqueous acetic acid. After cooling, the solid was removed by filtration, washed with acetone, and dried to yield 1.13 g (88%) of a mixture of **8** and **5**. NMR [$(CD_3)_2SO$] of the mixture showed resonances at δ 1.65 (s, CH_3), 1.75 (s, CH_3), 2.30 (s, pu-CH_3), 2.31 (s, pu-CH_3), 4.62 (d, pu-CH_2C), 4.82 (d, pu-CH_2C), 5.18 (m, C–CH=C), 6.42 (broad, pu-NH_2).

High-performance liquid chromatographic separation of a 50-mg sample of the mixture was done on Bio-Rad Aminex A-5 cation exchange resin, packed in a 15 × 0.5 in. glass column maintained at a temperature of 50°. The column was eluted at a flow rate of 700 μl/min (ca. 275 psi) with 0.50 *M* ammonium formate–formic acid buffer containing 25% dimethylformamide, pH 4.10 (calculated). The retention volume of the minor isomer was 172 ml. See below for characterization.

The major isomer was eluted with a retention volume of 235 ml to give 30 mg of colorless needles of **8**: mp >300°; λ_{max} (H_2O) 271 nm (ϵ 13400), 236 (7900); (H_2O, 0.1 *N* HCl) 267 (12900), 245 sh (8200); (H_2O, 0.1 *N* NaOH) 277 (14800); NMR [$(CD_3)_2SO$] δ 1.65 (s, 3, CH_3), 1.75 (s, 3, CH_3), 2.31 (s, 3, pu-CH_3), 4.62 (d, 2, pu-CH_2C), 5.18 (m, 1, C–CH=C), 6.72 (broad, 2, pu-NH_2); mass spectrum (10 eV) *m/e* 233 (M^+) and 265 $(M - C_5H_8)^+$; high-resolution mass spectrum *m/e* 233.1278 (calcd, $C_{10}H_{15}N_5O$).

Anal. Calcd for $C_{11}H_{15}N_5O$: C, 56.64; H, 6.48; N, 30.02. Found: C, 56.94; H, 6.42; N, 29.96.

8-Methyl-9-pivaloyloxymethylguanine (7). Sodium hydride (3.00 g of a 51% oil dispersion, 60 mmol) was washed with two portions of dry hexane (30 ml). A solution of 8-methylguanine (**6**, 5.00 g, 30 mmol) in dry dimethyl sulfoxide (100 ml) was then added to the sodium hydride, and the mixture was stirred at 30° for 6 hr. Chloromethyl pivalate (5.00 g, 33 mmol) was added, and the reaction mixture was stirred at 30° for an additional 2 hr. The solution was treated with charcoal and filtered, and the $(CH_3)_2SO$ was removed in vacuo. To the residue was added 30 ml of 20% acetic acid, and the resulting suspension was stirred for 30 min with cooling. The product was removed by filtration, washed with water and then acetone, and dried to give 7.06 g (92%) of colorless solid. An analytical sample was obtained by an additional recrystallization from methanol: mp >350°; λ_{max} (H_2O) 276 nm (ϵ 8900), 251 (13700); NMR [$(CD_3)_2SO$] δ 1.11 [s, 9, $C(CH_3)_3$], 2.35 (s, 3, pu-CH_3), 5.85 (s, 2, pu-CH_2O), 6.45 (broad, 2, pu-NH_2); mass spectrum (10 eV) *m/e* 255 (M^+), 170 $(M - C_5H_9O)^+$, and 140 $(M - C_6H_{10}O_2)^+$.

Anal. Calcd for $C_{12}H_{17}N_5O_3$: C, 51.61; H, 6.14; N, 25.07. Found: C, 51.61; H, 6.43; N, 25.18.

8-Methyl-7-(3-methyl-2-butenyl)guanine (5). To a suspension of 8-methyl-9-pivaloyloxymethylguanine (**7**, 150 mg, 0.59 mmol) in dry dimethylformamide (40 ml) was added isopentenyl bromide (175 mg, 12 mmol) and pyridine (0.5 ml). The mixture was stirred at room temperature for 200 hr. The DMF was removed in vacuo, and to the oily residue was added 20 ml of 2.0 *N* sodium hydroxide. This mixture was then heated on a steam bath for 1 hr. The basic solution was neutralized to pH 6, and the precipitate was collected and washed successively with ethanol and acetone. The light yellow solid was recrystallized from 80% ethanol–water to give 137 mg (55%) of yellow solid: mp >300°; λ_{max} (H_2O) 283 nm (ϵ 8590), 248 sh (6690); (H_2O, 0.1 *N* HCl) 276 (8470), 247 (12600); (H_2O, 0.1 *N* NaOH) 278 (8570); NMR [$(CD_3)_2SO$] δ 1.65 (s, 3, CH_3), 1.75 (s, 3, CH_3), 2.30 (s, 3, pu-CH_3), 4.82 (d, 2, pu-CH_2C), 5.18 (m, 1, C–CH=C), 6.32 (broad, 2, pu-NH_2); mass spectrum (10 eV) *m/e* 233 (M^+) and 265 $(M - C_5H_8)^+$.

Anal. Calcd for $C_{11}H_{15}N_5O \cdot \frac{1}{2}H_2O$: C, 54.55, H, 6.65; N, 28.93. Found: C, 54.55; H, 6.47; N, 28.82.

8-Methyl-9-(3-methyl-2-butenyl)guanine (10). Sodium hydride (0.60 g of a 51% oil dispersion, 12 mmol) was added to a vigorously stirred suspension of 8-methylguanine (**6**, 1.00 g, 6 mmol) in dry DMF (50 ml). This mixture was stirred for 3 hr. A solution of isopentenyl bromide (1.2 g, 8 mmol) in dry DMF (40 ml) was then added dropwise over a period of 5 hr, and the mixture was stirred for an additional 30 min. The solvent was removed in vacuo, and to the residue was added 10 ml of 2 *N* sodium hydroxide. The solution was then washed with two portions of ether (10 ml). The aqueous layer was neutralized to pH 6 with 20% acetic acid and cooled. The precipitate was collected by filtration and washed successively with ethanol and ether to yield 481 mg (36%) of yellow solid: mp >300°; λ_{max} (H_2O) 273 nm sh (ϵ 9670), 252 (13400); (H_2O, 0.1 *N* HCl) 277 (8770), 252 (1280); (H_2O, 0.1 *N* NaOH) 269 (11800), 255 sh (11300); NMR [$(CD_3)_2SO$] δ 1.65 (s, 3, CH_3), 1.75 (s, 3, CH_3), 2.27 (s, 3, pu-CH_3), 5.47 (d, 2, pu-CH_2C), 5.12 (m, 1, C–CH=C), 6.34 (broad, 2, pu-NH_2); mass spectrum (10 eV) 233 (M^+), and 165 $(M - C_5H_8)^+$.

Anal. Calcd for $C_{11}H_{15}N_5O$: C, 56.64; H, 6.48; N, 30.02. Found: C, 56.83; H, 6.22; N, 30.17.

8-Methyl-1-(3,methyl-2-butenyl)guanine (9). A solution of 8-methyl-9-pivaloyloxymethylguanine (**7**, 500 mg, 1.79 mmol) in dry dimethylformamide (200 ml) was treated with potassium *tert*-butoxide (250 mg, 2.23 mmol) under a nitrogen atmosphere. Isopentenyl bromide (425 mg, 2.85 mmol) was then added and the mixture stirred for 1 hr. Additional aliquots of potassium *tert*-butoxide (100 mg, 0.89 mmol) and isopentenyl bromide (100 mg, 0.67 mmol) were added, and the mixture was stirred for 1 hr. The dimethylformamide was then removed in vacuo, and the residue was dissolved in chloroform (100 ml) and filtered through a Celite pad. The chloroform solution was reduced in volume, applied to a 17-g silica gel column, and eluted with chloroform. The initial yellow fractions were discarded and the remaining fractions were concentrated to give 140 mg (23%) of crude 8-methyl-1-(3-methyl-2-butenyl)-9-pivaloyloxymethylguanine. This material was heated at reflux in 0.5 *N* sodium hydroxide–30% ethanol for 6 hr without further purification. After the solution was concentrated to 25 ml and made strongly acidic with 1 *N* HCl, it was extracted with three portions of $CHCl_3$ (30 ml). The aqueous layer was then neutralized with 1 *N* $NaHCO_3$ and the volume reduced to 5 ml. The resulting suspension was heated until the solid material dissolved and was treated with charcoal, filtered, and allowed to crystallize. The white crystals were filtered and dried to give 50 mg (53%) of **9**. An analytical sample was obtained by recrystallization from water: mp >300°; λ_{max} (H_2O) 275, 251 nm; (H_2O, 0.1 *N* HCl) 273 sh, 252; (H_2O, 0.1 *N* NaOH) 277, 262 sh; NMR [$(CD_3)_2SO$] δ 1.65 (s, 3, CH_3), 1.75 (s, 3, CH_3), 2.28 (s, 3, pu-CH_3), 4.56 (d, 2, pu-CH_2C), 5.10 (m, 1, C–CH=C), 6.50 (broad, 2, pu-NH_2); mass spectrum (10 eV) *m/e* 233 (M^+) and 265 $(M - C_5H_8)^+$.

Anal. Calcd for $C_{11}H_{15}N_5O \cdot \frac{1}{4}H_2O$: C, 55.51; H, 6.72; N, 29.44. Found: C, 55.55; H, 6.72; N, 29.18.

Acknowledgment. This work was supported by Research Grant MPS 74-05911 from the National Science Foundation. The authors are grateful to Dr. Charles R. Frihart for suggestions that stimulated this research.

Registry No.—**2**, 57346-44-8; **5**, 57346-45-9; **6**, 23662-75-1; **7**, 57346-46-0; **8**, 57346-47-1; **9**, 57346-48-2; **10**, 57346-49-3; 2-amino-

6-mercapto-8-methylpurine, 57379-36-9; 3-methyl-2-buten-1-ol, 556-82-1; chloromethyl pivalate, 18997-19-8.

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Reaction of 7,7,8,8-Tetracyanoquinodimethane with Sodium Benzoate and Acetone

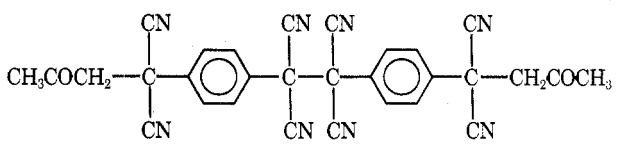
Malvina Farcasiu and Charlotte S. Russell*

Department of Chemistry, City College of the City University of New York, New York, New York 10031

Received August 27, 1975

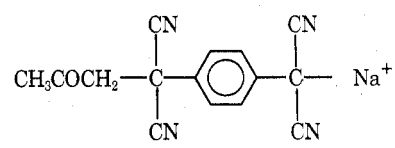
Complexes and anion radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) exhibit unusual electrical conductivity properties.[1] TCNQ forms π complexes[1,2] with Lewis bases, simple anion radical salts ($M^+TCNQ\cdot^-$) with metal iodides [except for $Cs_2(TCNQ\cdot^-)_2(TCNQ)$], and complex salts with organic iodides. Tropylium iodide reacts with $Li^+TCNQ\cdot^-$ to yield α,α'-ditropyl-$\alpha,\alpha,\alpha',\alpha'$-tetracyano-*p*-xylene. TCNQ undergoes 1,6 addition with sulfurous acid and with chlorine. When TCNQ reacts with primary and secondary amines, one or two cyano groups are replaced by amine.[3]

Although acetone has been used as a solvent in some of these reactions, no reaction of TCNQ with acetone has been reported. This work describes a unique reaction which produces an acetone-substituted dimer of TCNQ, I. It appears that carboxylate anion is oxidized by TCNQ because sodium benzoate, sodium salicylate, and sodium acetate reduced TCNQ to $Na^+TCNQ\cdot^-$ in acetone and generated acetonyl radical. However, little or no CO_2 was evolved in these reactions.

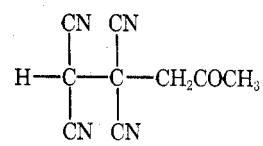


I

In a typical experiment TCNQ (20.0 mmol) and sodium benzoate (20.0 mmol) in 500 ml of dry acetone were stirred vigorously at room temperature in the dark for 48 hr. Results were the same in air and under nitrogen. $Na^+TCNQ\cdot^-$ (6.7 mmol) and benzoic acid (10.0 mmol) were obtained, as well as 0.319 g of compound I (dimer) and 1.736 g of compound II. The latter was soluble in ethyl acetate, ethanol, and acetonitrile with a light green color. II had strong absorption at 320 nm and very weak, broad absorption at 500–600 nm. II had strong infrared absorption (KBr disk) at 2130 and 2170 cm^{-1} (substituted malononitrile anion as in sodium pentacyanoethane and potassium phenylmalononitrile),[4] weak absorption at 2250 cm^{-1} (unconjugated nitrile with electronegative groups on carbon), strong absorption at 1720 cm^{-1} (ketone), and peaks at 1610, 1520, 825 (para-substituted phenyl with strong π overlap), 1420, 1360 cm^{-1} (methyl and methylene). The NMR spectrum in acetone-d_6 showed two coupled doublets, 7.3 (2 H) and 7.0 ppm (2 H), and two singlets, 3.8 (2 H) and 2.3 ppm (3 H). When TCNQ was added to II, $Na^+TCNQ\cdot^-$ was formed. We assign to II the structure i on the basis of evidence described above, the conversion to dimer described below, and the fact that ii is formed from tetracyanoethylene and



i



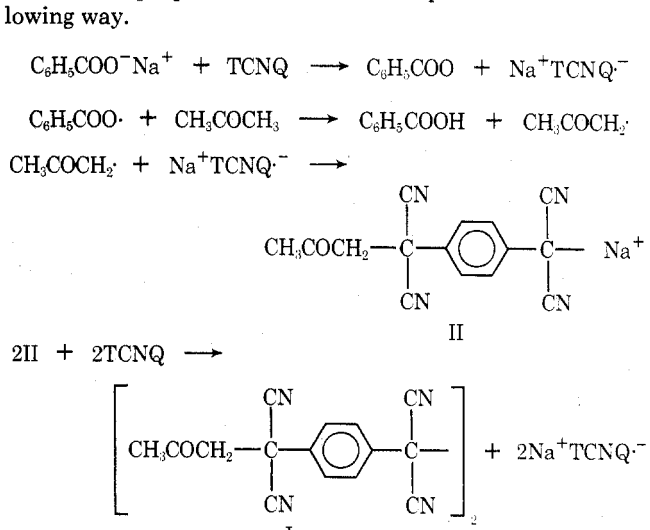
ii

acetone by a free-radical mechanism.[5,6] II is also formed when sodium acetate and sodium salicylate were used instead of sodium benzoate.

An equimolar mixture of II and TCNQ in ethyl acetate yielded $Na^+TCNQ\cdot^-$ and I. I was purified by washing with ethanol and recrystallization from acetone, white needles, mp 279.9–280.1°C. I had a maximum at 320 nm in ethanol. The infrared spectrum (KBr disk) showed strong absorption at 1730 cm^{-1} (ketone) and very weak absorption at 2250 and 2350 (unconjugated nitrile with electronegative groups on α carbon as in *p*-phenylenemalononitrile, which has a band at 2270 cm^{-1}), 1510 and 805 (para-substituted phenyl), and 1425 and 1355 cm^{-1} (methyl and methylene). The NMR spectrum in acetone-d_6 showed two coupled doublets, 7.9 (2 H) and 7.6 ppm (2 H), and singlets at 4.0 (2 H) and 2.3 ppm (3 H). Anal. Calcd for $C_{30}H_{18}O_2N_8$: C, 69.0; H, 3.5; N, 21.5. Found: C, 68.8; H, 3.4; N, 21.4. Mol wt: calcd, 522; found, 483. The mass spectrum at high gain shows a peak at *m/e* 522.

When acetonitrile was used as solvent in this reaction, $Na^+TCNQ\cdot^-$ was produced along with a material with broad absorption at 365 and 390 nm which resisted purification. With sodium carbonate and acetone or acetonitrile, TCNQ was converted to the sodium salt of α,α-dicyano-*p*-toluoyl cyanide.[3]

We assign to I the structure of the dimer rather than monomer primarily because of the molecular weight determination. We propose that the reaction proceeds in the following way.



I