photocopy or $2.00 for microfiche, referring to code number JOC-74-1466.

References and Notes

(1) Research supported by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.
(2) Presented at the 24th Southeastern Regional Meeting of the American Chemical Society, Birmingham, Ala., Nov. 2–4, 1972.
(3) B. C. Pal, M. Uziel, D. G. Doherty, and W. E. Cohn, *J. Amer. Chem. Soc.*, **91**, 3634 (1969).
(4) See paragraph at end of paper regarding supplementary material.
(5) Lack of quantitative conversion of VII to VI may be due to the instability of 6-mercaptopurine in alkali noted earlier. 6-Mercaptopurine is converted to purine 6-sulfinate in better than 60% yield in dilute alkaline solution (30–50 μM) for 96 hr [I. L. Doerr, I. Wempen, D. A. Clarke, and J. J. Fox, *J. Org. Chem.*, **26**, 3401 (1961)].
(6) M. Saneyoshi and S. Nishimura, *Biochim. Biophys. Acta*, **204**, 389 (1970).
(7) R. T. Walker, *Tetrahedron Lett.*, **No. 24**, 2145 (1971).
(8) Y. Degani and A. Patchornik, *J. Org. Chem.*, **36**, 2727 (1971).
(9) W. O. Foye, A. M. Hebb, and J. Mickles, *J. Pharm. Sci.*, **56**, 292 (1967).
(10) R. T. Walker and U. L. RajBhandary, *J. Biol. Chem.*, **247**, 4879 (1972).
(11) M. Saneyoshi and G. Chihara, *Chem. Pharm. Bull.*, **15**, 909 (1967).
(12) J. J. Fox, D. V. Praag, I. Wempen, I. L. Doerr, L. Cheong, J. E. Knoll, M. L. Eidinoff, A. Bendich, and G. B. Brown, *J. Amer. Chem. Soc.*, **81**, 178 (1959).

Ultraviolet- and γ-Ray-Induced Reactions of Nucleic Acid Constituents. Reactions of Purines with Ethers and Dioxolane

David Leonov and Dov Elad*

Department of Organic Chemistry, The Weizmann Institute of Science, Rehovot, Israel

Received August 23, 1973

Ultraviolet- and γ-ray-induced reactions of caffeine, adenine, and guanosine with tetrahydrofuran, tetrahydropyran, dioxane, tetrahydrofurfuryl alcohol, and dioxolane are described. The reactions lead to the appropriate 8-substituted purines in yields of up to 90% when performed in the presence of photoinitiators. A free-radical mechanism is proposed for these reactions.

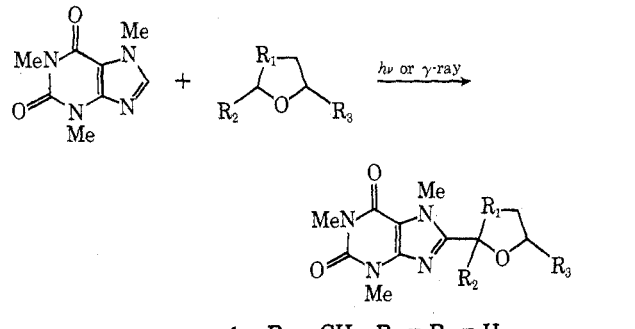
Ultraviolet and γ-ray-induced reactions of purines with alcohols or amines have been described recently.[1] These reactions resulted in the substitution of the appropriate moiety for the 6- or 8-hydrogen atom in the purine system. Thus, in reactions of purines with alcohols the substituent was usually the α-hydroxyalkyl group, while with amines it was the α-aminoalkyl group. The reactions could be induced directly with ultraviolet light (λ >260 nm) or by the use of photosensitizers (with light of λ >290 nm), which increased the yields of the photoproducts.

The aim of the present study is the investigation of the photochemical reactions of purines with a variety of substrates, mainly with those present in living systems. This will contribute to a better understanding of the photochemical reactions of purines, and subsequently to the development of selective photochemical reactions for these moieties in nucleic acids. In addition, it is anticipated that this study will shed further light on the interaction under irradiation of nucleic acids with their environment. The photoreactions of purines with ethers[2] and acetals serve as models for the interaction of purines with sugars and might lead to the discovery of new, so far unknown, irradiation-induced modifications in nucleic acids. The present publication includes full details of the photochemical and γ-ray-induced reactions of purines and purine nucleosides with a variety of ethers, hydroxy ethers, and dioxolane. An attempt was made to carry out the reactions under conditions in which purine moieties in nucleic acids would react selectively; therefore, photosensitizers which have been shown previously to induce selective reactions of purines,[3] *e.g.*, peroxides, were employed.

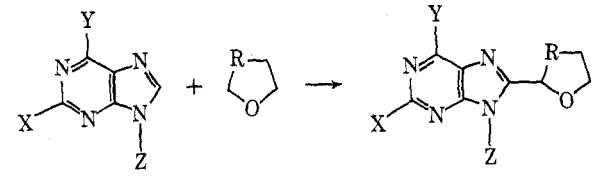
Results and Discussion

Irradiation with ultraviolet light or exposure to γ rays of caffeine, adenine, or guanosine with ethers, hydroxy ethers, or dioxolane led to the substitution of the appropriate moiety for the hydrogen atom at the 8 position of the purine. The site of binding to the purine in the ether moiety is at the carbon atom α to the ether oxygen,[2] whereas with dioxolane it is at the acetalic carbon. The reactions studied can be presented as shown in Scheme I.

Scheme I



1, $R_1 = CH_2$; $R_2 = R_3 = H$
2, $R_1 = O$; $R_2 = R_3 = H$
3a, $R_1 = CH_2$; $R_2 = H$; $R_3 = CH_2OH$
3b, $R_1 = CH_2$; $R_2 = CH_2OH$; $R_3 = H$
4a, $R_1 = CH_2$; $R_2 = H$; $R_3 = CH_2OCOCH_3$
4b, $R_1 = CH_2$; $R_2 = CH_2OCOCH_3$; $R_3 = H$
5, $R_1 = CH_2O$; $R_2 = R_3 = H$
6, $R_1 = (CH_2)_2$; $R_2 = R_3 = H$



X = H; Y = NH_2; Z = H (adenine)
X = NH_2; Y = OH; Z = ribose (guanosine)

7, R = CH_2
8, R = O
9, R = CH_2O
10, R = $(CH_2)_2$
11, R = CH_2
12, R = $(CH_2)_2$

The reactions could be either induced directly by ultraviolet light (λ >260 nm) or through photochemical initiation with peroxides (with light of λ >290 nm) with higher yields of the photoproducts. Products were isolated by column chromatography using a modified "dry column" technique[4] followed by elution with acetone–petroleum ether mixtures for the caffeine derivatives, and methanol–

Table I
Photochemical and γ-Ray-Induced Reactions of Caffeine, Adenine, and Guanosine with Ethers, Hydroxy Ethers, and Dioxolane

Purine	Substrate	Reaction conditions	Product	Product mp, °C	Yield, %[a]
Caffeine	THF[b]	Caffeine (0.5 g), water (10 ml), THF (140 ml), DBP[c] (6 ml); 6 hr	**1**	128–129	90
	THF[d]	Caffeine (0.5 g), water (10 ml), THF (200 ml), DBP (8 ml); 8 days	**1**		50
	THF[e]	Caffeine (1 g), water (20 ml), THF (120 ml); 48 hr	**1**		50
	Tetrahydropyran[b]	Caffeine (3 g), water (10 ml), tetrahydropyran (110 ml), *tert*-butyl alcohol (30 ml), DBP (8 ml); 21 hr	**6**	160–161	74
	Dioxane[f]	Caffeine (1 g), water (10 ml), dioxane (140 ml); 168 hr	**5**	201–202	43
	Dioxane[b]	Caffeine (2 g), water (15 ml), dioxane (120 ml), DBP (8 ml); 24 hr	**5**		73
	Dioxane[e]	Caffeine (1 g), water (20 ml), dioxane (120 ml); 48 hr	**5**		50
	Tetrahydrofurfuryl alcohol[b]	Caffeine (2 g), water (20 ml), tetrahydrofurfuryl alcohol (120 ml), DBP (6 ml); 24 hr	**3a**	90–91	58
			3b	191–192	23
	Tetrahydrofurfuryl acetate[b]	Caffeine (3.2 g), water (15 ml), tetrahydrofurfuryl acetate (120 ml), DBP (10 ml); 24 hr	**4a**	89–90	60
			4b	187–180	22
	Dioxolane[b]	Caffeine (0.4 g), water (10 ml), dioxolane (50 ml), DBP (6 ml); 4 hr	**2**	215–216	55
	Dioxolane[d]	Caffeine (0.5 g), water (10 ml), dioxolane (100 ml), DCP[g] (6 g); 8 days	**2**		67
Adenine	THF[f]	Adenine (1 g), water (30 ml), THF (120 ml); 48 hr	**7**	290–291	40
	THF[b]	Adenine (1 g), water (30 ml), THF (120 ml), DBP (6 ml); 20 hr	**7**		90
	THF[d]	Adenine (0.5 g), water (20 ml), THF (200 ml), DCP (6 g); 16 days	**7**		80
	THF[e]	Adenine (2.03 g), water (50 ml), THF (360 ml); 64 hr	**7**		60
	Tetrahydropyran[b]	Adenine (1 g) water (30 ml), tetrahydropyran (70 ml), *tert*-butyl alcohol (50 ml), DBP (8 ml); 28 hr	**10**	305–306	44
	Dioxane[b]	Adenine (2 g), water (100 ml), dioxane (600 ml), DBP (10 ml); 60 hr	**9**	328–329	58
	Dioxolane[b]	Adenine (1 g), water (30 ml), dioxolane (120 ml), DBP (8 ml); 14 hr	**8**	267–268	90
Guanosine	THF[b]	Guanosine (1.5 g), water (100 ml), THF (650 ml), DBP (15 ml); 52 hr	**11**	190–191 dec	67
	Tetrahydropyran	Guanosine (1.3 g), water (90 ml), tetrahydropyran (500 ml), *tert*-butyl alcohol (150 ml), DBP (10 ml); 168 hr	**12**	264–265 dec	60

[a] Based on reacted purines (conversions usually ranged from 50 to 90%). [b] Hanovia 450-W high-pressure mercury vapor lamp (Pyrex filter). [c] DBP, di-*tert*-butyl peroxide. [d] In sunlight. [e] With γ rays. ^{60}Co source Gammacell 220 (Atomic Energy of Canada Ltd., Ottawa, Canada); dose rate 12,000 rads/min. [f] Corex filter. [g] DCP, dicumyl peroxide.

chloroform for the other purine derivatives. Progress of the reactions was followed by thin-layer chromatography and more quantitatively by nmr measurements. In the latter, the disappearance of the H-8 absorption band of the purine with the simultaneous appearance of the absorption of the protons of the substituent at C-8 could be followed. Our results are summarized in Tables I and II.

All new photoproducts gave correct analytical data for the proposed structures and were characterized by their uv, nmr, and mass spectra. The nmr spectra of the caffeine photoproducts exhibited the three characteristic singlets of the *N*-methyl groups at the τ 6–7 region. The substitution at the C-8 position of the caffeine was indicated by the absence of the H-8 absorption in the photoproducts. Determination of the site of attachment in the ether or acetal moieties to the C-8 position of caffeine was also made through the nmr spectra of the products. The absorption at lowest field (τ 4.82 for the hydroxy ether or its acetate, and τ 3.95 for dioxolane) is attributed to the proton attached to the carbon atom of the ether or the acetal moiety which is bound to the C-8 position of caffeine. It appears as a multiplet in the hydroxy ethers and as a singlet in the dioxolane photoproduct, which is in agreement with the proposed structures. The absorption bands of the other protons in the ether or acetal moiety are similar to those of the starting ether or acetal. Substitution in adenine also occurred at the C-8 position, as the photoproducts possessed only one band (singlet) at the τ 2 region, which was not changed by treatment with D_2O at 105°.[5] The site of binding in the ether or acetal moiety was also determined by nmr spectra as described above and was shown to be the carbon atom α to the ether oxygen or at the acetalic carbon, respectively. All guanosine photoproducts do not possess the absorption band of the H-8 proton in the nmr, thus indicating that the hydrogen atom at C-8 was substituted. The absorption of the sugar moiety in the photoproduct is very similar to that of the starting nucleotide, except for the anomeric proton.[1b] The

Table II
Analytical and Nmr Data of 8-Substituted Purines

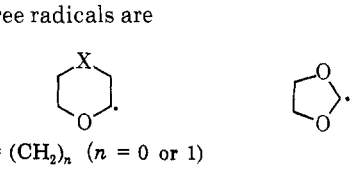
Compound	Elemental analysis[a]	Solvent[b]	Nmr spectrum τ values
2	Calcd for $C_{11}H_4N_4O_4$: C, 49.62; H, 5.31; N, 20.25; mol wt, 266. Found: C, 49.62; H, 5.30; N, 21.04; mol wt, 266	A	3.95 (s, 1 H, O–CH–O), 5.82 (m, 4 H, $-CH_2CH_2-$), 5.95 (s, 3 H, N-7 CH_3), 6.45 (s, 3 H, N-3 CH_3), 6.64 (s, 3 H, N-1 CH_3)
3a	Calcd for $C_{13}H_{18}N_4O_4 \cdot H_2O$: C, 50.0; H, 6.40; N, 17.93; mol wt, 294 + 18. Found: C, 50.15; H, 6.47; N, 17.93; mol wt, 294	A	4.82 (m, 1 H, caffeine CH–O), 5.7 (m, 1 H, $-CHCH_2OH$) 6 (d, 3 H, N-7 CH_3; J = 3.6 Hz), 6.28 (m, 2 H, $-CH_2OH$), 6.46 (s, 3 H, N-3 CH_3), 6.64 (s, 3 H, N-1 CH_3), 7.68 (br m, 4 H, $-CH_2CH_2-$)
3b	Calcd for $C_{13}H_{18}N_4O_4$: C, 53.05; H, 6.16; N, 19.04; mol wt, 294. Found: C, 53.06; H, 6.28; N, 18.81; mol wt, 294	A	5.8 (s, 3 H, N-7 CH_3), 6.02 (m, 2 H, CH_2O), 6.2 (s, 2 H, CH_2OH), 6.47 (s, 3 H, N-3 CH_3), 6.63 (s, 3 H, N-1 CH_3), 7.75 (br m, 4 H, CH_2CH_2-)
4a	Calcd for $C_{15}H_{20}N_4O_5$: C, 53.56; H, 5.99; N, 16.66. Found: C, 53.80; H, 6.12; N, 16.82	A	4.83 (m, 1 H, –CHO), 5.78 (m, 3 H, –CHO + CH_2CO-), 5.94 (s, 3 H, N-7 CH_3), 6.42 (s, 3 H, N-1 CH_3), 7.47 (br m, 7 H, $-COCH_3$ + $-CH_2CH_2-$)
4b	Calcd for $C_{15}H_{20}N_4O_5$: C, 53.56; H, 5.99; N, 16.66. Found: C, 53.43; H, 6.16; N, 16.43	A	5.84 (s, 3 H, H-7 CH_3), 6.02 (m, 2 H, $-CH_2O$), 6.21 (m, 2 H, $-CH_2OCO-$), 6.5 (s, 3 H, N-3 CH_3), 6.67 (s, 3 H, N-1 CH_3), 8 (br m, 7 H, $-COCH_3$ + $-CH_2CH_2-$)
7	Calcd for $C_9H_{11}N_5O$: C, 52.47; H, 5.56; N, 34.03; mol wt, 205. Found: C, 52.67; H, 5.40; N, 34.13; mol wt, 205	B	1.73 (s, 1 H, C-2 H), 2.73 (s, 2 H, $-NH_2$), 4.1 (t, 1 H, OCH, J = 6.5 Hz), 6.02 (m, 2 H, CH_2O), 7.92 (br m, 4 H, $-CH_2CH_2-$)
8	Calcd for $C_8H_9N_5O_2 \cdot H_2O$: C, 42.66; H, 4.92; N, 31.1; mol wt, 207 + 18. Found: C, 42.37; H, 5.05; N, 31.34; mol wt, 207	B	1.77 (s, 1 H, C-2 H), 2.69 2 H, $-NH_2$), 4.0 (s, 1 H, –CHO), 5.87 (d, 4 H, $-CH_2CH_2-$)
9	Calcd for $C_9H_{11}N_5O_2$: C, 48.70; H, 4.99; N, 31.46; mol wt, 221. Found: C, 48.86; H, 5.01; N, 31.66; mol wt, 221	B	1.82 (s, 1 H, C-2 H), 2.86 (s, 2 H, $-NH_2$), 5.12 (m, 1 H, –CHO), 6.15 (m, 6 H, $-CH_2O$)
10	Calcd for $C_{10}H_{13}N_5O$: C, 54.78; H, 5.93; N, 31.95; mol wt, 219. Found: C, 55.02; H, 5.80; N, 32.2; mol wt, 219	B	1.85 (s, 1 H, C-2 H), 2.95 (s, 2 H, $-NH_2$), 5.4 (m, 1 H, CHO), 6.07 (m, 2 H, CH_2O), 8.3 (br m, 6 H, $-CH_2CH_2CH_2-$)
11	Calcd for $C_{14}H_{19}N_5O_6 \cdot H_2O$: C, 45.28; H, 5.70; N, 18.86. Found: C, 45.42; H, 5.67; N, 18.95	B	3.58 (s, 2 H, $-NH_2$), 4.11 (apparent d, 1 H, H-1′), 4.83 (br m, 4 H, OH-3′, OH-2′, OH-5′, –CHO), 5.82 (m, 2 H, CH_2O), 6.2 (m, 4 H, H-3′, H-4′, 2 H-5′), 8 (br m, 4 H, $-CH_2CH_2-$)
12	Calcd for $C_{15}H_{21}N_5O_6$: C, 49.04; H, 5.76; N, 19.07. Found: C, 48.82; H, 5.92; N, 18.97	B	3.65 (s, 2 H, $-NH_2$), 4.12 (apparent d, 1 H, H-1′), 4.73 (m, 1 H, OH-3′), 5.05 (m, 2 H, OH-2′, OH-5′), 5.45 (m, 1 H, CHO), 5.78 (m, 2 H, CH_2O), 6.32 (m, 5 H, H-2′, H-3′, H-4′, 2H-5′), 8.26 [broad m, 6 H, $(CH_2)_3$]

[a] Molecular weights were determined by mass spectrum. [b] A is $CDCl_3$; B is $(CD_3)_2SO$.

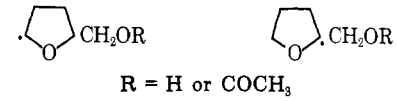
presence of an absorption of a single proton in the tetrahydropyranyl derivative at τ 5.54 indicates that substitution in tetrahydropyran occurred at the carbon atom α to the ether oxygen. In the tetrahydrofuranyl side chain the absorption of the methine proton was hidden by that of the hydroxylic protons of the sugar moiety (at τ 4.83). All other tetrahydropyranyl and tetrahydrofuranyl protons exhibited absorption bands similar to those of the parent ethers.

All caffeine photoproducts exhibited a strong molecular peak in their mass spectra, except **4a** and **4b**. In these compounds the ester was decomposed to the appropriate alcohol and to ketene.[6] Their mass spectra are similar, therefore, to those of **3a** and **3b**, respectively. A fragment common to all caffeine photoproducts is that of m/e 194, which is the fragment of the caffeine moiety. Other typical fragments of ether or acetal entities attached to the C-8 position, and of other caffeine moieties, were also observed.[2,7] Adenine photoproducts exhibited the appropriate molecular peaks and a common fragment of the adenine moiety at m/e 135. Other fragments are typical of ether or acetal and of adenine fragmentations.[5] The guanosine photoproducts did not exhibit molecular peaks in their spectra. It is interesting to note that guanosine itself does not show a molecular peak under the same conditions of recording. A typical fragmentation pattern of ribose nucleosides was observed in these spectra, *i.e.*, peaks of B + H, B + 24, B + 30, and M + 89 (B represents the mass of the free base with the ether or the acetal moiety attached at the C-8 position minus one).[8]

The reported reactions could be induced by light of λ >260 nm (Corex filter) or λ >290 nm (Pyrex filter) in the presence of photosensitizers. In the former case, the purine serves as the light absorbing system and the excited purine abstracts a hydrogen atom from the hydrogen donor forming a free radical of the latter. This radical is scavenged by a neighbor purine molecule which subsequently yields the appropriate photoproduct. In the peroxide-initiated reactions, most of the incident light (λ >290 nm) is absorbed by the photoinitiator[1e] which decomposes to oxy radicals which subsequently abstract a hydrogen atom from the α position of the ether or the acetal. The resultant free radicals are



X = $(CH_2)_n$ (n = 0 or 1)



R = H or $COCH_3$

The next step involves the attack of an ether or acetal free radical on the carbon end of the C-8=N-7 bond of a ground state purine molecule leading to a radical which by further hydrogen atom abstraction yields the N-7, C-8 adducts ("dihydro" type). These are then oxidized to yield the appropriate C-8 substituted purine.[1b] The free radical nature of the reactions is indicated by the possible induction of the reactions with peroxides, either photochemically or thermally. Further evidence for such a mechanism is derived from the formation of dehydro dimers, of the ethers, such as dioxanyl-dioxane in the reaction mixture. The quantum yields of the peroxide-induced reactions of caffeine were measured by the ferrioxalate method[9] and were found to be *ca.* 5×10^{-2}.

The reactions described in this publication can serve as models for the interaction of purines and sugars in photochemical reactions. They also have an implication on the possible cross linking of nucleic acids and sugars through the purine moieties. In addition, the reactions of the acetal can serve as a means for the introduction of an aldehydic group at the C-8 position of the purines in nucleic acids. The resulting aldehyde may be useful for the cross linking with other functional groups (*e.g.*, amino groups) in the nucleic acid chain or in proteins.

Experimental Section

Caffeine (Schuchardt, München) was recrystallized from water prior to use. Other purines (Fluka, CHR grade) were used without further purification. Ethers (Frutarom), tetrahydrofurfuryl alcohol (Fluka), and dioxolane (Fluka) were freshly distilled before use. Kieselgel (0.063–0.2 mm Merck) was used for column chromatography. Progress of the reactions were followed by ascending tlc on aluminum plates (Riedel-de-Haen, Kieselgel SIF). Acetone-petroleum ether mixtures were used as eluents for the caffeine derivatives, and methanol-chloroform for the adenine and guanosine derivatives. Spots were detected by mineralight lamp. Column chromatography was performed on silica gel (Kieselgel 60, Merck) using a modified "dry column" technique.[4] Nmr spectra were determined with a Varian A-60 instrument in the appropriate organic solvent using TMS as internal standard. Mass spectra were recorded with a MAT Atlas CH4. Uv spectra were recorded on a Cary 14 spectrophotometer.

Irradiations were carried out in an immersion apparatus with internal water cooling using Hanovia 450-W high-pressure mercury vapor lamps as the light source. The irradiation vessel was flushed with oxygen-free nitrogen for 15 min prior to irradiation, and nitrogen bubbling, as well as mechanical stirring, were sustained throughout the irradiation. Quantum yields were measured by ferrioxalate actinometry.[9] γ-Ray irradiation was conducted in a Gammacell 220 apparatus (Atomic Energy of Canada Ltd. Ottawa, Canada), with an internal air cooling device, and at a dose rate of 12,000 rads/min. Oxygen-free nitrogen was bubbled through the solution.

Typical experiments are described. Other experiments were conducted under similar conditions and are summarized in Tables I and II. Unless otherwise stated, Pyrex filters were employed.

Reaction of Caffeine and 1,3-Dioxolane (with DBP). A mixture of caffeine (0.4 g), dioxolane (50 ml), and water (10 ml) was irradiated for 4 hr, while DBP (total amount 6 ml) was added periodically in small portions. Excess reagent was removed under reduced pressure, and the residue was chromatographed on silica gel (100 g). Acetone-petroleum ether (3:17) eluted **2** (0.25 g), mp 215–216° (from acetone-petroleum ether).

Reaction of Adenine and THF (with DBP). A mixture of adenine (1 g), water (30 ml), and THF (120 ml) was irradiated for 20 hr, while DBP (6 ml) was added in small portions. The usual work-up and chromatography led to **7** [0.56 g; eluted with methanol-chloroform (1:9)], mp 290–291° (from chloroform-methanol).

Reaction of Guanosine and THF (with DBP). A solution of guanosine (1.5 g), water (100 ml), and THF (650 ml) was irradiated for 52 hr. DBP (15 ml) was added periodically in small amounts. The usual work-up led to **11** [0.91 g; eluted with methanol-chloroform (1:9)], mp 190–191° dec (from methanol-chloroform).

Registry No.—**1**, 27077-61-8; **2**, 51015-44-2; **3a**, 51015-45-3; **3b**, 51015-56-6; **12**, 51015-57-7; caffeine, 58-08-2; adenine, 73-24-5; guanosine, 118-00-3; 1,3-dioxolane, 646-06-0; tetrahydrofuran, 109-51015-56-6; **12**, 51015-57-7; caffeine, 58-08-2; adenine, 73-24-5; guanosine, 118-00-3; 1,3-dioxolane, 646-06-0; tetrahydrofuran, 109-99-9; tetrahydropyran, 142-68-7; dioxane, 123-91-1; tetrahydrofurfuryl alcohol, 97-99-4; tetrahydrofurfuryl acetate, 637-64-9.

References and Notes

(1) (a) J. S. Connolly and H. Linschitz, *Photochem. Photobiol.*, **7**, 791 (1968); (b) H. Steinmaus, I. Rosenthal, and D. Elad, *J. Amer. Chem. Soc.*, **91**, 4921 (1969); *J. Org. Chem.*, **36**, 3594 (1971); (c) B. Evans and R. Wolfenden, *J. Amer. Chem. Soc.*, **92**, 4751 (1970); (d) N. C. Yang, L. S. Gorelic, and B. Kim, *Photochem. Photobiol.*, **13**, 275 (1971); (e) J. Salomon and D. Elad, *Tetrahedron Lett.*, 4783 (1971); *Photochem. Photobiol.*, **19**, 21 (1974).
(2) S. Jerumanis and A. Martel, *Can. J. Chem.*, **48**, 1716 (1970).
(3) D. Leonov, J. Salomon, S. Sasson, and D. Elad, *Photochem. Photobiol.*, **17**, 465 (1973).
(4) B. Loev and M. M. Goodman, *Intra-Sci. Chem. Rep.*, **4**, 283 (1970).
(5) J. M. Rice and G. O. Dudek, *J. Amer. Chem. Soc.*, **89**, 2719 (1967).
(6) K. Biemann, "Mass Spectrometry-Chemical Applications," McGraw-Hill, New York, N. Y., 1962, p. 111; J. Collin, *Bull. Soc. Chim. Belg.*, **69**, 449 (1960).
(7) Z. Voticky, V. Kovacik, A. Rybar, and K. Antas, *Collect. Czech. Chem. Commun.*, **34**, 1657 (1969).
(8) K. Bieman and J. A. McCloskey, *J. Amer. Chem. Soc.*, **84**, 2005 (1962).
(9) C. A. Parker, *Proc. Roy. Soc., Ser. A*, **220**, 104 (1953).