Headline Articles

Aromatic Nitration under Neutral Conditions Using Nitrogen Dioxide and Ozone as the Nitrating Agent. Application to Aromatic Acetals and Acylal

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Cyclic acetals derived from aromatic carbonyl compounds can be nitrated smoothly with nitrogen dioxide in ice-cooled dichloromethane or acetonitrile in the presence of ozone and magnesium oxide to give *ortho*- and *para*-nitro derivatives as the major product in good combined yields, the acetal ring as a protective group remaining almost intact. An acylal derived from benzaldehyde similarly undergoes nitration on the aromatic ring to give an isomeric mixture of three nitro compounds, in which the *ortho* and *meta* isomers predominate, while aromatic orthoesters are rapidly decomposed to give simply the parent esters. Ring nitration under neutral conditions has been interpreted in terms of a nonclassical mechanism, in which nitrogen trioxide is involved as the initial electrophile.

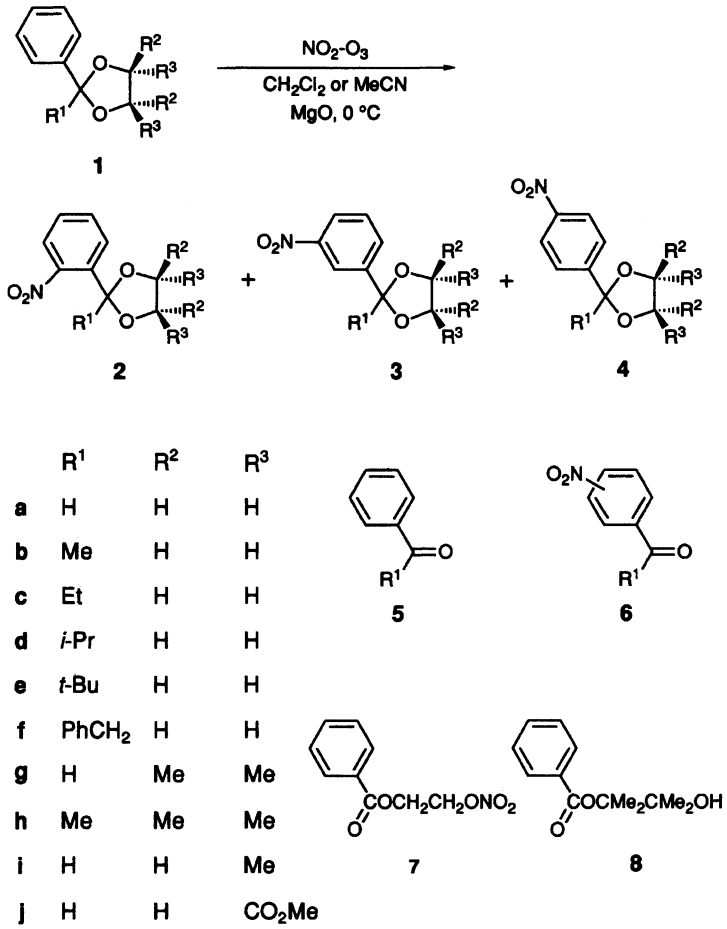
Aromatic nitro compounds are usually prepared by treatment of arenes with nitric acid or a mixture of nitric acid and sulfuric acid (mixed acid). Since the first discovery by E. Mitscherlich in 1834,[1] this methodology has over a century been the only one that one can usefully employ for introducing the nitrogen atom or atoms directly into an aromatic nucleus. Various aspects of such aromatic nitration are now well-understood in terms of a single reaction mechanism involving the nitronium ion (NO_2^+) as the universal electrophile.[2] Since it is a strong Lewis acid, the nitronium ion requires strong acidic conditions for its generation. Aromatic nitration must therefore be carried out using concentrated nitric acid or nitric acid–sulfuric acid as the nitrating agent.

Recently, we have discovered an alternative type of electrophilic aromatic nitration which can be conducted satisfactorily under neutral conditions, i.e., the ozone-mediated nitration of arenes with lower oxides of nitrogen (referred to as *Kyodai*-nitration).[3] The reaction is most likely to proceed via the nitrogen trioxide (NO_3) as the initial electrophile, which is a highly electron-deficient neutral radical species not requiring acidic conditions for its generation.[4] In this paper, we report the results of our efforts to apply this novel type of reaction to the nuclear nitration of acid-sensitive aromatic compounds such as acetals, acylal, and orthoesters.

Results and Discussion

***Kyodai*-Nitration of Aromatic Acetals.** Acetals are widely used as a masked carbonyl function in organic synthesis, since they are easily hydrolyzed by the action of weak acid to generate the original aldehyde or ketone.[5] It is quite understandable, therefore, that we find no reports of the successful nitration of aromatic acetals in the literature, because electrophilic nitrating agents would prefer the acetal oxygen atoms to the less basic aromatic ring carbons at initial stage, thus facilitating the subsequent nucleophilic cleavage of the C–O bond.

When aromatic acetals were subjected to the *Kyodai*-nitration, we were pleased to see that some cyclic acetals **1c—e** could be successfully nitrated on the aromatic ring to give the corresponding nitration products **2—4** in good yields, the acetal ring as a protecting function remaining almost intact (Scheme 1; Table 1). Thus, a mixture of acetal **1**, magnesium oxide as an acid scavenger, and dichloromethane or acetonitrile as solvent was stirred vigorously at 0 °C, while ozonized oxygen and nitrogen dioxide mixed immediately before were bubbled slowly into the chalky suspension. The reaction proceeded smoothly and the expected nitration products, mainly composed of *ortho*- and *para*-nitro derivatives, were obtained in good yields after the usual workup.



	R^1	R^2	R^3
a	H	H	H
b	Me	H	H
c	Et	H	H
d	*i*-Pr	H	H
e	*t*-Bu	H	H
f	$PhCH_2$	H	H
g	H	Me	Me
h	Me	Me	Me
i	H	H	Me
j	H	H	CO_2Me

Scheme 1.

Table 1. Nitration of Cyclic Acetals **1**

Acetal	Nitration product yield (%)[a]	Isomer proportion (%)[b] **2** : **3** : **4**
In dichloromethane at 0 °C		
1a	0[c]	— : — : —
1b	4[c,d]	31 : 19 : 50
1c	58	22 : 19 : 59
1d	88	18 : 20 : 62
1e	93	6 : 25 : 69
1g	0[e]	— : — : —
1h	90	8 : 13 : 79
In acetonitrile at 0 °C		
1a	0[c]	— : — : —
1b	2[c,d]	23 : 30 : 47
1c	95	14 : 31 : 55
1d	88	12 : 29 : 59
1e	90	7 : 31 : 62
1g	0[e]	— : — : —

a) The yields refer to isomeric mixtures isolated and were not optimized. b) Isomer proportions were determined by GLC. c) Deacetalization preceded the nuclear nitration. d) Accompanied by small amounts of the nitrate ester **7**, in addition to the unmasked ketone **5b** and its nitration product **6b**. e) Readily cleaved to give 3-benzoyloxy-2,3-dimethylbutan-2-ol **8** as the main product.

"Crowdedness" around the acetal carbon is crucial for the successful nitration of cyclic acetals **1**. When the "less crowded" acetals **1a**,**b** and **1i** were allowed to react under similar conditions, extensive or complete cleavage of the acetal ring occurred in preference to the nuclear nitration, to give a mixture of the original carbonyl compounds **5a**,**b**, nitro derivatives **6a**,**b** and other products, the ratios of which varied considerably depending on the conditions employed. With the "moderately crowded" acetals **1c**—**e**, satisfactory results were obtained, the yields of the nitration products being in the range of 58—95%. Nitration of these acetals by the conventional procedure based on the use of nitric acid–sulfuric acid always led to the nitration products **6** of the original carbonyl compounds, as expected. Alternatively, the attempted reaction with nitric acid in acetic anhydride led to a complex mixture of products probably arising from the acid-catalyzed acetal-acylal exchange and subsequent reactions.

In the *Kyodai*-nitration of acetals **1b**,**c**, small amounts of a nitrate ester **7** were formed as a by-product, showing the complicated nature of the reaction. Compound **7** was isolated by chromatography on silica gel and confirmed by direct comparison with the authentic specimen prepared by an independent route. Although the mechanistic pathway leading to the es-

ter **7** is not clear at present, the cation radical species is a probable intermediate for such ester formation, as will be discussed later. The *Kyodai*-nitrations run in acetonitrile appeared to give somewhat better results than those run in dichloromethane, since the formation of dinitration products was reduced appreciably in the former solvent system.

When the ethylenedioxy group in acetal **1b** was replaced by the more bulky 1,1,2,2-tetramethylethylenedioxy group, the cleavage of the 1,3-dioxolane ring was effectively suppressed and the expected nitration products **2h**—**4h** were obtained in a good combined yield. Although the protection of acetophenone with pinacol (2,3-dimethylbutane-1,2-diol) led to satisfactory results in the *Kyodai*-nitration, a similar protection of benzaldehyde failed to produce any promising results. 3-Benzoyloxy-2,3-dimethylbutan-2-ol **8** was isolated as the sole product in 80—90% yield when acetal **1g** was treated either with ozone[6] or with nitrogen dioxide[7] alone under the similar conditions. Such facile ozonolytic cleavage of the acetal ring may be interpreted in terms of the stereoelectronic orbital interaction between the ozone and the acetal function.[6]

In an attempt to avoid such facile ozone-induced, oxidative cleavage of the acetal function, nitrogen dioxide and ozonized oxygen were blown into a suspension of magnesium oxide in acetonitrile, while the substrate was added simultaneously to the reaction system at an appropriate rate. This reverse addition proved to be successful and the nitration products **2g**—**4g** were obtained in an acceptable combined yield. The formation of ester **8** was suppressed under these conditions. Some results obtained from **1g** according to this type of reverse addition procedure are shown in Table 2, although no efforts were made to optimize the yields.

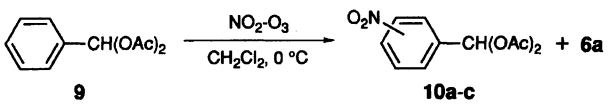
When the more bulky dimethyl (*R*,*R*)-tartrate was introduced in place of pinacol for the protection of benzaldehyde, the resulting acetal **1j** smoothly underwent *Kyodai*-nitration without cleavage of the acetal bond to give a mixture of the expected nitration products **2j**—**4j** in 85% isolated yield. Overcrowding around the acetal carbon atom brought by the two neighboring methoxycarbonyl groups at 4,5-positions of 1,3-dioxolane ring as well as their electron-withdrawing effect would prevent the attachment of electrophile to the acetal oxygen atoms,[8] thus favoring the ring substitution over the oxidative cleavage of the acetal function. As shown in Table 2, the nuclear nitration of acetal **1j** occurred mainly at the *ortho*- and *meta*-positions rather than the *ortho*- and *para*-positions. This may be taken to indicate that the 1,3-dioxolan-2-yl substituent in **1j** is less electron-donating, probably due to the combined inductive electron withdrawal by the two methoxycarbonyl groups. A higher proportion of the *ortho* isomer, as compared with the results from **1g**, may be attributed to interaction between the attacking electrophile and the ester function, as has been observed in the *Kyodai*-nitration of aromatic ketones.[9]

Acyclic acetals such as benzaldehyde diethyl acetal and acetophenone dimethyl acetal were rapidly cleaved under our conditions to afford the expected nitration product of the original aldehyde or ketone. The isomer proportions of the products were almost the same as those obtained from the *Kyodai*-nitration of the respective carbonyl compounds **5**.

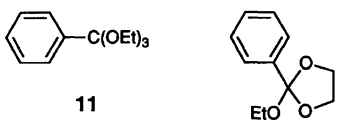
***Kyodai*-Nitration of Aromatic Acylal 9.** Acylal is another type of the masked carbonyl function, which tolerates mild acidic conditions. Compound **9** was smoothly nitrated with the present nitrating system to give product **10** in 64% isolated yield (Scheme 2). Addition of magnesium oxide did not improve the results. The isomer distribution of the product **10** was *ortho* 55 (**10a**), *meta* 28 (**10b**) and *para* 17% (**10c**), reflecting the increased electron-attracting nature of the acylal group, $CH(OCOMe)_2$, as compared with the acetal function, $CH(OR)_2$. Some interaction between the ester oxygen atoms and attacking electrophile may be responsible again for the high *ortho* isomer ratio. The attempted nitration of acylal **9** using the classical procedure based on nitric acid–sulfuric acid only resulted in the production of nitrobenzaldehydes **6a** (93% isolated yield), mainly composed of the *meta* isomer.

Attempted *Kyodai*-Nitration of Aromatic Orthoesters 11 and 12. The orthoester function is highly acid-sensitive and readily converted to the ester function under acidic conditions. Thus the literature to date contains no reports on the nitration of aromatic orthoesters. As expected, the attempted *Kyodai*-nitration of compound **11** resulted in the immediate decomposition to ethyl benzoate. Similar attempts to nitrate the cyclic orthoester **12** led to the ring opening, giving the nitrate ester **7** as the major product.

Acetal Function as the Substituent Group. No information is available to date on the directing property of the acetal function as a ring substituent for the nitration of arenes. As shown above, although the acetal function directs an entering electrophile mainly at *ortho* and *para* positions, substitution at *meta* position is also appreciable, probably due to the joint electron withdrawal by two geminal alkoxy groups. The partial rate factors of compound **1e** were determined



9 **10a-c**



11 **12**

Scheme 2.

Table 2. Nitration of Cyclic Acetals of Benzaldehyde in Acetonitrile at 0 °C

Entry	Acetal	Time[a] min	Product yield (%)[b]	Isomer proportion (%)[c] **2** : **3** : **4**	Yield of ester **8** (%)
1	**1a**	—	0	— : — : —	—
2	**1g**	—	0	— : — : —	68
3	**1g**	10	40	34 : 24 : 42	18
4	**1g**	40	61	34 : 24 : 42	5
5	**1g**	40[d]	44	34 : 24 : 42	22
6	**1i**	—	0	— : — : —	—
7	**1j**	—	85	43 : 41 : 16	—

a) In entries 3—5, the solution in which nitrogen dioxide and ozone had been reacted was left with stirring for the indicated time before acetal **1g** and magnesium oxide was introduced (reverse addition method). Entries 1,2,6, and 7 were run according to the typical procedure detailed in the Experimental. b,c) See footnotes in Table 1. The yields were not optimized. d) Before the addition of acetal and magnesium oxide, argon gas was bubbled through the solution for this length of time in order to remove the unreacted nitrogen oxide.

by the competition method to be $f_o=0.20$, $f_m=0.62$, and $f_p=3.2$ (Table 3). The values revealed that the acetal function is comparable in its electronic influence with the chloromethyl group ($f_o=0.72$, $f_m=0.30$, and $f_p=2.24$) and cyanomethyl group ($f_o=0.25$, $f_m=0.21$, and $f_p=1.15$).[10] The low f_o value is attributable to the bulky *t*-butyl group in compound **1e**. Stepwise substitution of one, two or three chlorine atoms into the methyl group in toluene is known to bring a gradual change-over of the directing effect from mainly *ortho/para* to mainly *meta*. Thus, on nitration with nitric acid–sulfuric acid, benzyl chloride gives an isomeric mixture in which the *ortho–para* nitro derivatives predominate ($o:m:p=34:14:53$);[10] in contrast, α,α,α-trichlorotoluene affords the *m*-nitro derivative as the major product ($o:m:p=7:65:29$).[11] As far as can be judged from the proportion of the *meta* isomer, the dialkoxymethyl group may be regarded as less electronegative than the dichloromethyl and bis(acetoxy)methyl groups, their respective electron-withdrawing abilities being in the order $CH(OR)_2<CH(OCOMe)_2<CHCl_2$.

Mechanism for the Fragmentation of Acetals. For the ozone-mediated nitration of arenes, we have proposed a mechanism in which the reaction proceeds in a dual mode depending on the oxidation potential of aromatic substrate;[4] nitrogen dioxide reacts with ozone to give nitrogen trioxide (Eq. 1), which oxidizes aromatic substrate (ArH) to form cation radical ($ArH^{+\bullet}$) (Eq. 2) as an intermediate to ring substitution (Eq. 3). In the absence of an appropriate oxidizable substrate, nitrogen trioxide is trapped by another molecule of nitrogen dioxide to form dinitrogen pentaoxide, which is a powerful nitrating agent in the presence of acid catalyst (Eq. 4).

$$NO_2 + O_3 \longrightarrow NO_3 + O_2 \quad (1)$$

$$ArH + NO_3 \longrightarrow ArH^{+\cdot} + NO_3^- \quad (2)$$

$$ArH^{+\cdot} + NO_2 \longrightarrow Ar(H)NO_2^+ \xrightarrow{-H^+} ArNO_2 \quad (3)$$

$$NO_2 + NO_3 \longrightarrow N_2O_5 \xrightarrow{H^+} NO_2^+ + HNO_3 \quad (4)$$

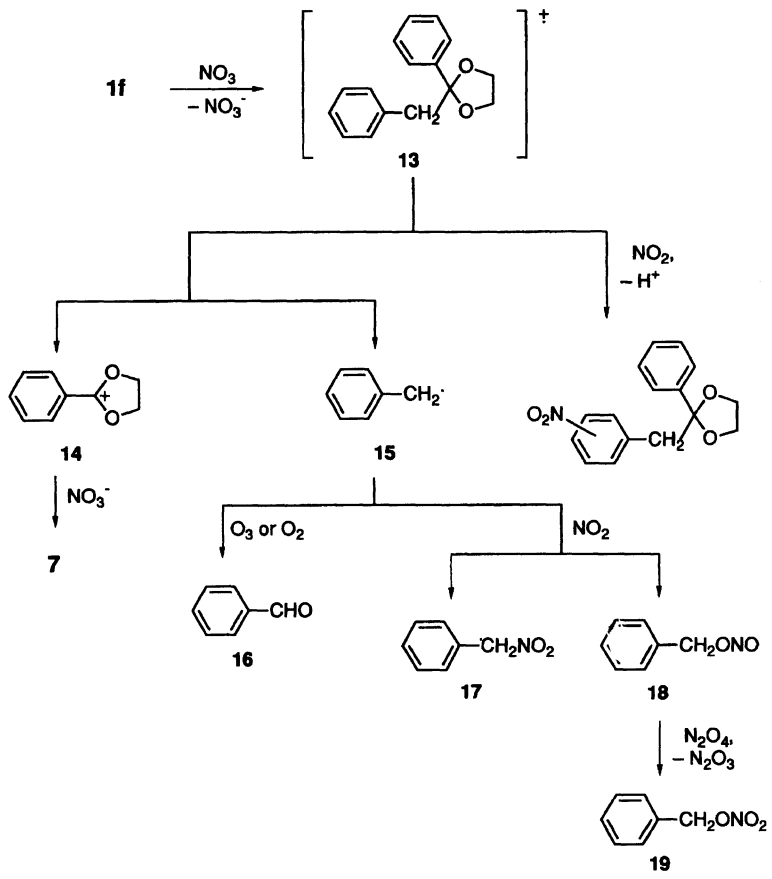
Table 3. Partial Rate Factors of Cyclic Acetals **1**[a]

Acetal	k_R/k_B	f_o	f_m	f_p
1c	0.42	0.31	0.25	1.4
1d	0.69	0.35	0.44	2.6
1e	0.81	0.20	0.62	3.2

a) Reactions were carried out at 0 °C using a mixture of acetal (2.5 mmol), benzene (2.5 mmol), cyclododecane (0.022 mmol; internal standard), magnesium oxide (0.30 g) and dichloromethane (50 ml). Product determinations were made by GLC at a stage of about 15% conversion.

According to the above mechanism, the 1,3-dioxolane ring is oxidized by nitrogen trioxide to form its cation radical, which would suffer fragmentation into the alkyl or aryl radical and 1,3-dioxolan-2-ylium cation, as shown in Scheme 3.[12] Thus, the *Kyodai*-nitration of acetal **1f** first produces cation radical **13**, which undergoes fragmentation into 2-phenyl-1,3-dioxolan-2-ylium cation **14** and benzyl radical **15**.[13] The latter radical is oxidized to form benzaldehyde **16**, or trapped by nitrogen dioxide to form nitrophenylmethane **17** and benzyl nitrite **18**. The latter compound undergoes facile oxidation to benzyl nitrate **19**. The cation **14** is trapped by nitrate anion to open the 1,3-dioxolane ring to produce the nitrate ester **7**. The last type of reaction of the 1,3-dioxolan-2-ylium cation salt has many precedents.[14] The same nitrate **7** was also obtained in a small amount in the nitration of acetals **1b** and **1c**. These findings clearly endorse the conclusion that the cation radical species is involved in the *Kyodai*-nitration of electron-rich aromatic substrates.

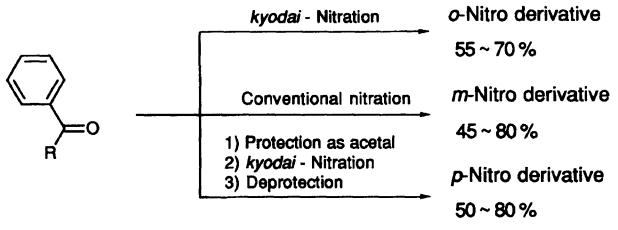
Potentials in Organic Synthesis. Conventional nitration of benzaldehyde and alkyl phenyl ketones by nitric acid–sulfuric acid leads mainly to the *meta*-isomers, the *ortho* isomer being the next major product. In contrast, the *Kyodai*-nitration of these carbonyl com-



Scheme 3.

pounds gives mainly the *ortho* isomer, the *meta* isomer being the second important.[9] In both cases, the formation of the *para* isomer is insignificant. The *para*-nitro derivatives of these carbonyl compounds are usually prepared by way of multistep routes involving acetoacetate ester synthesis,[15] malonic ester synthesis,[16] oxidation of 1-alkyl-4-nitroarenes,[17] or nitration of 1-phenylalkyl acetates.[18] Since further structural elaboration of cyclic acetals would improve the product yields, the nitration of cyclic acetals according to the present procedure provides a novel route to this class of compounds, noteworthy for its manipulative simplicity and easy access to starting materials of major industrial importance.

In conclusion, by a proper choice of the nitration methodology (conventional or *Kyodai*) and carbonyl substrate (unmasked or masked), we are now able to obtain either one of the desired isomers as the major product from the nitration of aromatic aldehydes and ketones (Scheme 4).



Scheme 4.

Experimental

Melting points were determined on a Yanagimoto hot-stage apparatus. All melting and boiling points are not corrected. IR spectra were recorded on a Shimadzu FTIR-8100S infrared spectrophotometer as liquid films or KBr pellets. ^{1}H NMR spectra were measured on a Varian Gemini-200 (200 MHz) spectrometer for $CDCl_3$ solutions, with tetramethylsilane as the internal standard. Coupling constants J are given in Hz. Mass spectra were recorded on a Shimadzu GCMS QP2000A spectrometer at an ionization potential of 70 eV. GLC analyses were carried out on a Shimadzu GC-14A gas chromatograph, using a CBP-1-M25-025 column [25 m×0.2 mm (i.d.)]. Merck precoated silica gel sheets 60F-254 were used for TLC. Column chromatography was performed on a Wakogel 200 (100—200 mesh) using hexane - ethyl acetate as eluent. Preparative liquid chromatograph Shimadzu LC-8A was employed for the separation of the products, using a Shimadzu SHIM-PACK PRC-ODS column [250 mm×20 mm (i.d.)]. Products were identified by IR, ^{1}H NMR, MS, and elemental analysis, or by direct comparison with the authentic specimens prepared by an independent route. All solvents used were reagent-grade commercial products. Dichloromethane and acetonitrile were dried by distillation from calcium hydride. Nitrogen dioxide (99% pure) was purchased in a cylinder from Sumitomo Seika Co., Ltd. and used after transfer distillation. Ozone was generated from a Nippon Ozone Co.,

Ltd., type ON-1-2 apparatus, which produced ozone at a rate of 10 mmol h^{-1} under an oxygen flow of 10 $dm^3 h^{-1}$ and an applied voltage of 80 V.

Preparation of Aromatic Acetals. Method A (Acetalization).[19] **Typical Procedure.** A solution of pivalophenone **5e** (9.25 g, 45 mmol), ethylene glycol (4.95 g, 80 mmol), and *p*-toluenesulfonic acid (0.08 g) in dry benzene (30 cm^3) was heated at reflux using a Dean–Stark trap for concomitant removal of water. When the theoretical amount of water was collected, the reaction mixture was cooled to room temperature and treated with aqueous $NaHCO_3$. The organic layer was separated, washed with brine, and dried over anhydrous Na_2SO_4. After the removal of solvent, the residue was recrystallized from hexane to give acetal **1e**; yield 9.20 g (84%). Other acetals **1a—d,f,h,i** were all prepared in a similar manner.

Method B (Transacetalization).[8b] **Typical Procedure.** A mixture of acetophenone dimethyl acetal (6.64 g, 40 mmol),[20] pinacol (5.73 g, 47 mmol), and *p*-toluenesulfonic acid (0.12 g) was stirred at 80 °C and the liberated methanol was distilled off from the reaction mixture. The residue was extracted with dichloromethane and the extract was washed successively with aqueous $NaHCO_3$ and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was distilled under reduced pressure to afford acetal **1g**; yield: 6.11 g (69%).

Preparation of (Diacetoxymethyl)benzene (9).[21] A solution of benzaldehyde (6.36 g, 50 mmol) in acetic anhydride (18 ml) was stirred at 0 °C for 15 min and then anhydrous $FeCl_3$ (0.12 g) was added. After another 30 min at 0 °C, the reaction mixture was diluted with water and the organic phase was extracted with hexane (30 ml). The extract was dried over anhydrous Na_2SO_4. After removal of the solvent, the residual solid was recrystallized from hexane to give acylal **9**; yield 9.12 g (73%). Mp 45—46 °C (lit,[21] 44—46 °C); IR (KBr) 1752, 1376, 1245, 1209, 1012, 949, 762, and 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.12 (6H, s), 7.3—7.6 (5H, m), and 7.68 (1H, s); MS (EI) *m/z* 165 (M^+-43; 4.5), 149 (2.5), 123 (2.0), 107 (23), 105 (43), 77 (20), 51 (11), and 43 (100).

Preparation of Orthoesters. Triethyl Orthobenzoate (11): Sodium metal (3.74 g, 163 mmol) was carefully dissolved in absolute ethanol (50 ml) cooled in an ice bath. When the gas evolution ceased, benzotrichloride (9.78 g, 50 mmol) was added dropwise to the solution at 0 °C. The resulting mixture was stirred for 2 h at room temperature, and then heated under reflux for 27 h. The mixture was cooled in the ice-bath and the precipitated NaCl was removed by filtration. The filtrate was evaporated to leave an oily residue, which was distilled under reduced pressure to give orthoester **11** as a colorless oil (lit,[22] bp 114—115 °C (25 mmHg, 1 mmHg=133.322 Pa)); yield 7.99 g (71%).

2-Ethoxy-2-phenyl-1,3-dioxolane (12): A mixture of triethyl orthobenzoate **11** (6.72 g, 30 mmol), ethylene glycol (1.90 g, 31 mmol) and *p*-toluenesulfonic acid (0.09 g) was heated at 100 °C and the liberated ethanol was slowly distilled off from the reaction mixture. The residue was subsequently distilled under reduced pressure to give orthoester **12** as an oil (lit,[23] bp 121—126 °C (12 mmHg)); yield 3.03 g (52%).

Nitration of Aromatic Acetals 1a-e,g-j. Typical Procedure. In a three-necked 50 cm^3 flask fitted with a gas inlet tube and a vent that allows waste gas to escape was placed 2-*t*-butyl-2-phenyl-1,3-dioxolane **1e** (2.06 g, 10 mmol), magnesium oxide (0.60 g, 15 mmol), and freshly distilled acetonitrile (50 cm^3). The mixture was cooled to 0 °C with stirring in an ice bath, and the ozonized oxygen and nitrogen dioxide mixed immediately before were slowly bubbled into the chalky suspension through the gas inlet tube. The progress of the reaction was monitored by GLC. After 1.5 h the reaction mixture was quenched by the addition of aqueous $NaHCO_3$. The organic layer was extracted with dichloromethane, washed with brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated to leave a mixture of nitrated acetals **2e—4e** as a pasty solid. The yield and isomer ratio of the product determined by GLC were 90% and *o*:*m*:*p*=7:31:62. Each isomer was isolated by preparative liquid chromatography on a reversed-phase column using 70% MeOH– 30% H_2O solution as the eluent.

Nitration of 4,4,5,5-Tetramethyl-2-phenyl-1,3-dioxolane (1g). Ozonized oxygen was bubbled through for 2 h in dry acetonitrile (50 cm^3), while liquid nitrogen dioxide (2.0 cm^3) was added in four portions (0.5 $cm^3 \times 4$) at intervals of 30 min. After the final addition, the mixture was stirred for 10—40 min; then magnesium oxide (0.60 g, 15 mmol) followed by acetal **1g** (2.06 g, 10 mmol) was added. The reaction mixture was stirred for an additional 30 min and then worked up as described above. The respective yields of the nitration products **2g—4g** and ester **8** were determined by GLC.

Nitration of 2-Benzyl-2-phenyl-1,3-dioxolane (1f). To a stirred mixture of acetal **1f** (1.20 g, 5 mmol), magnesium oxide (0.30 g, 7.5 mmol) and freshly distilled dichloromethane (50 cm^3) was added liquid nitrogen dioxide (0.5 cm^3). Ozonized oxygen was slowly introduced into the suspension and the aliquots withdrawn every 15 min were analyzed by GLC. After 45 min, the reaction was quenched by the addition of water; then the reaction mixture was worked up as usual. The combined yield of the nitration products **2f—4f** determined by GLC was 49%, while the yields of nitrate **7**, benzaldehyde **16**, nitrophenylmethane **17**, and benzyl nitrate **19** were estimated by ^1H NMR to be 44, 15, 4, and 10%, respectively; in both determinations cyclododecane was used as the internal standard.

Nitration of (Diacetoxymethyl)benzene (9). Acylal **9** (2.12 g, 10 mmol) was dissolved in freshly distilled dichloromethane (50 cm^3). Nitrogen dioxide and ozonized oxygen were separately introduced into the solution and the aliquots withdrawn every 30 min were analyzed by GLC. The yields of the nitrated products **10a—c** were determined by GLC using dodecane as the internal standard.

Attempted Nitration of Triethyl Orthobenzoate (11). Magnesium oxide (0.30 g, 7.5 mmol) was suspended in a solution of orthoester **11** (1.13 g, 5 mmol) in freshly distilled acetonitrile (50 cm^3), and a gaseous mixture of ozonized oxygen and nitrogen dioxide was introduced slowly into the suspension with vigorous stirring. After 1 h the reaction mixture was worked up as usual. Inspection by GLC and ^1H NMR revealed that ethyl benzoate was the sole product obtained.

Preparation of 2-(Benzoyloxy)ethyl Nitrate (7). Ethylene chlorohydrin (2.01 g, 25 mmol) and pyridine (2.05 g, 25 mmol) were dissolved in dry dichloromethane (50 cm^3); to this solution benzoyl chloride (3.51 g, 25 mmol) was added

slowly with vigorous stirring. After 2 h, the reaction was quenched by adding aqueous HCl. The organic layer was separated, washed with aqueous $NaHCO_3$ and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated and the residue was distilled under reduced pressure to give 2-chloroethyl benzoate in 58% yield.

A mixture of the benzoate thus obtained (0.92 g, 5 mmol), silver nitrate (1.27 g, 7.5 mmol) and dry acetonitrile (15 cm^3) was stirred at 50 °C for 4 d, during the course of which silver chloride slowly precipitated. After the disappearance of the substrate on TLC, aqueous NaCl was added and the precipitated silver chloride was removed by filtration. The organic layer was extracted with dichloromethane, washed successively with aqueous $NaHCO_3$, water and brine, and dried over Na_2SO_4. After removal of the solvent, the remaining nitrate ester **7** was purified by chromatography (yield; 0.66 g, 63%).

Spectral data, mps and bps of new compounds as well as those of less common compounds are shown below.

2-Phenyl-1,3-dioxolane (1a). Bp 113—115 °C (16 mmHg) (lit,[24] 115—116 °C (16 mmHg)); IR (neat) 1397, 1314, 1275, 1221, 1094, 1071, 1028, and 967 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.0—4.2 (4H, m), 5.82 (1H, s), and 7.3—7.5 (5H, m); MS(EI) m/z 150 (M^+; 3.4), 149 (14), 123 (38), 105 (100), and 77 (63).

2-Methyl-2-phenyl-1,3-dioxolane (1b). Mp 62—63 °C (from ethanol) (lit,[8c] 57—58 °C); IR (KBr) 1439, 1372, 1221, 1024, 949, 870, and 768 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.66 (3H, s), 3.7—3.9 (2H, m), 3.9—4.1 (2H, m), 7.2—7.4 (3H, m), and 7.4—7.6 (2H, m); MS(EI) m/z 149 (M^+ −15; 100), 105 (72), 87 (46), and 77 (42).

2-Methyl-2-(2-nitrophenyl)-1,3-dioxolane (2b). Mp 60—62 °C (from hexane); IR (KBr) 1538, 1374, 1235, 1205, 1196, 1028, 878, and 785 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.86 (3H, s), 3.6—3.8 (2H, m), 3.9—4.1 (2H, m), 7.4—7.6 (3H, m), and 7.6—7.7 (1H, m); MS(EI) m/z 194 (M^+ −15; 100), 150 (41), 104 (12), 87 (49), and 76 (16). Found: C, 57.26; H, 5.19; N, 6.56%. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70%.

2-Methyl-2-(3-nitrophenyl)-1,3-dioxolane (3b). Mp 71—72 °C (from ethanol); IR (KBr) 1526, 1354, 1339, 1206, 1030, 876, and 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.67 (3H, s), 3.7—3.9 (2H, m), 4.0—4.2 (2H, m), 7.53 (1H, t, J=8.0 Hz), 7.83 (1H, dt, J=8.0 and 1.2 Hz), 8.16 (1H, ddd, J=8.0, 2.1, and 1.2 Hz), and 8.36 (1H, t, J=2.1 Hz); MS(EI) m/z 194 (M^+ −15; 100), 178 (2.8), 150 (51), 104 (21), 87 (51), and 76 (18). Found: C, 57.21; H, 5.43; N, 6.62%. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70%.

2-Methyl-2-(4-nitrophenyl)-1,3-dioxolane (4b). Mp 76—77 °C (from hexane–ethyl acetate); IR (KBr) 1522, 1347, 1198, 1032, 945, 884, and 845 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.54 (3H, s), 3.8—3.9 (2H, m), 4.0—4.1 (2H, m), 7.66 (2H, d, J=8.9 Hz), and 8.20 (2H, d, J=8.9 Hz); MS(EI) m/z 194 (M^+ −15; 100), 178 (1.6), 150 (34), 104 (18), 87 (38), and 76 (14). Found: C, 57.23; H, 5.29; N, 6.61%. Calcd for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70%.

2-Ethyl-2-phenyl-1,3-dioxolane (1c). Bp 111—113 °C (16 mmHg) (lit,[8c] 101.5—103 °C (11 mmHg)); IR (neat) 1449, 1293, 1225, 1186, 1049, 945, 758, and 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, J=7.4 Hz), 1.92 (2H, q, J=7.4 Hz), 3.7—3.9 (2H, m), 3.9—4.1 (2H, m), 7.2—7.4 (3H, m), and 7.4—7.5 (2H, m); MS(EI) m/z 149 (M^+ −29; 100), 105 (73), 101 (11), and 77 (41). Found: C, 73.85; H, 8.09%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92%.

2-Ethyl-2-(2-nitrophenyl)-1,3-dioxolane (2c). Mp 75—76 °C (from hexane–ethyl acetate); IR (KBr) 1541, 1372, 1206, 1034, 934, and 787 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.97 (3H, t, J=7.4 Hz), 2.17 (2H, q, J=7.4 Hz), 3.6—3.8 (2H, m), 3.9—4.1 (2H, m), 7.3—7.6 (3H, m), and 7.6—7.8 (1H, m); MS(EI) m/z 194 (M^+ −29; 100), 150 (27), 104 (12), 101 (15), and 76 (13). Found: C, 59.08; H, 5.82; N, 6.26%. Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27%.

2-Ethyl-2-(3-nitrophenyl)-1,3-dioxolane (3c). Oil; IR (neat) 1530, 1350, 1221, 1186, 1049, 938, 812, and 739 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (3H, t, J=7.4 Hz), 1.93 (2H, q, J=7.4 Hz), 3.7—3.9 (2H, m), 4.0—4.1 (2H, m), 7.53 (1H, t, J=7.9 Hz), 7.79 (1H, dt, J=7.9 and 1.2 Hz), 8.16 (1H, ddd, J=7.9, 2.2, and 1.2 Hz) and 8.33 (1H, t, J=2.2 Hz); MS(EI) m/z 194 (M^+ −29; 100), 150 (43), 104 (23), 101 (14), and 76 (20). Found: C, 59.39; H, 5.96; N, 6.15%. Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27%.

2-Ethyl-2-(4-nitrophenyl)-1,3-dioxolane (4c). Mp 80—81 °C (from hexane); IR (KBr) 1520, 1350, 1221, 1040, 936, 851, and 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (3H, t, J=7.4 Hz), 1.91 (2H, q, J=7.4 Hz), 3.7—3.9 (2H, m), 3.9—4.1 (2H, m), 7.63 (2H, d, J=8.6 Hz), and 8.20 (2H, d, J=8.6 Hz); MS(EI) m/z 194 (M^+ −29; 100), 150 (30), 104 (20), 101 (11), and 76 (13). Found: C, 59.11; H, 5.96; N, 6.18%. Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27%.

2-Isopropyl-2-phenyl-1,3-dioxolane (1d). Bp 119—120 °C (16 mmHg); IR (neat) 1474, 1447, 1383, 1227, 1090, 1022, 953, 752, and 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (6H, d, J=6.9 Hz), 2.13 (1H, sept, J=6.9 Hz), 3.7—3.8 (2H, m), 3.9—4.1 (2H, m), and 7.2—7.5 (5H, m); MS(EI) m/z 149 (M^+ −43; 100), 105 (55), and 77 (33). Found: C, 74.81; H, 8.52%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

2-Isopropyl-2-(2-nitrophenyl)-1,3-dioxolane (2d). Mp 63—64 °C (from hexane); IR (KBr) 1528, 1370, 1209, 1080, 953, 853, 783, and 745 cm^{-1}; ^1H NMR ($CDCl_3$) δ= 0.97 (6H, d, J=6.9 Hz), 2.57 (1H, sept, J=6.9 Hz), 3.6—3.8 (2H, m), 3.8—4.0 (2H, m), and 7.3—7.6 (4H, m); MS(EI) m/z 194 (M^+ −43; 100), 150 (21), 104 (12), and 76 (12). Found: C, 60.88; H, 6.31; N, 5.88%. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90%.

2-Isopropyl-2-(3-nitrophenyl)-1,3-dioxolane (3d). Mp 65—66 °C (from hexane–ethyl acetate); IR (KBr) 1532, 1354, 1115, 1022, 1003, 822, and 743 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (6H, d, J=6.9 Hz), 2.14 (1H, sept, J=6.9 Hz), 3.7—3.9 (2H, m), 3.9—4.1 (2H, m), 7.51 (1H, t, J=7.9 Hz), 7.76 (1H, dt, J=7.9 and 1.2 Hz), 8.15 (1H, ddd, J=7.9, 2.1, and 1.2 Hz), and 8.33 (1H, t, J=2.1 Hz); MS(EI) m/z 194 (M^+ −43; 100), 150 (35), 104 (21), and 76 (17). Found: C, 60.86; H, 6.35; N, 5.92%. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90%.

2-Isopropyl-2-(4-nitrophenyl)-1,3-dioxolane (4d). Mp 89—90 °C (from hexane); IR (KBr) 1518, 1348, 1138, 1100, 1008, 932, and 862 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (6H, d, J=6.9 Hz), 2.13 (1H, sept, J=6.9 Hz), 3.7—3.9 (2H, m), 3.9—4.1 (2H, m), 7.61 (2H, d, J=8.9 Hz), and 8.19 (2H, d, J=8.9 Hz); MS(EI) m/z 194 (M^+ −43; 100), 150 (22), 104 (18), and 76 (10). Found: C, 60.94; H, 6.44; N, 5.89%. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90%.

2-*t*-Butyl-2-phenyl-1,3-dioxolane (1e). Mp 67—68 °C (from hexane); IR (KBr) 1485, 1200, 1121, 750, and

710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96 (9H, s), 3.6—3.8 (2H, m), 3.8—4.0 (2H, m), 7.3—7.4 (2H, m), and 7.4—7.5 (3H, m); MS(EI) *m/z* 191 (M^+-15; 1.7), 149 (M^+-57; 100), 105 (45), and 77 (26). Found: C, 75.52; H, 8.99%. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79%.

2-*t*-Butyl-2-(2-nitrophenyl)-1,3-dioxolane (2e). Mp 111—112 °C (from hexane); IR (KBr) 1549, 1379, 1119, 1009, 980, and 776 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.02 (9H, s), 3.6—3.8 (2H, m), 3.8—4.0 (2H, m), 7.1—7.3 (1H, m), 7.3—7.5 (2H, m), and 7.5—7.6 (1H, m); MS(EI) *m/z* 194 (M^+-57; 100), 150 (20), 104 (12), and 76 (10). Found: C, 62.01; H, 6.92; N, 5.62%. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57%.

2-*t*-Butyl-2-(3-nitrophenyl)-1,3-dioxolane (3e). Mp 88—89 °C (from hexane–ethyl acetate); IR (KBr) 1530, 1348, 1119, 1022, 986, 968, and 739 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96 (9H, s), 3.6—3.8 (2H, m), 3.9—4.1 (2H, m), 7.48 (1H, t, *J*=7.9 Hz), 7.79 (1H, dt, *J*=7.9 and 1.2 Hz), 8.15 (1H, ddd, *J*=7.9, 2.1, and 1.2 Hz), and 8.32 (1H, t, *J*=2.1 Hz); MS(EI) *m/z* 236 (M^+-15; 2.4), 194 (M^+-57; 100), 150 (26), 104 (14), and 76 (11). Found: C, 62.13; H, 6.87; N, 5.51%. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57%.

2-*t*-Butyl-2-(4-nitrophenyl)-1,3-dioxolane (4e). Mp 118—119 °C (from hexane–ethyl acetate); IR (KBr) 1526, 1347, 1107, 1009, 943, 866, and 853 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96 (9H, s), 3.6—3.8 (2H, m), 3.9—4.1 (2H, m), 7.63 (2H, d, *J*=8.9 Hz), and 8.16 (2H, d, *J*=8.9 Hz); MS(EI) *m/z* 236 (M^+-15; 2.7), 194 (M^+-57; 100), 150 (23), 104 (18), and 76 (9.7). Found: C, 62.12; H, 6.97; N, 5.41%. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57%.

2-Benzyl-2-phenyl-1,3-dioxolane (1f).[13] Mp 83—84 °C (from hexane–ethyl acetate); IR (KBr) 1447, 1264, 1150, 1048, 1026, 984, 776, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.18 (2H, s), 3.7—3.9 (4H, m), and 7.1—7.4 (10H, m); MS(EI) *m/z* 149 (M^+-91; 100), 105 (68), 91 (12), and 77 (39). Found: C, 79.76; H, 6.71%. Calcd for $C_{13}H_{18}O_2$: C, 79.97; H, 6.71%.

4,4,5,5-Tetramethyl-2-phenyl-1,3-dioxolane (1g).[25] Bp 139—140 °C (23 mmHg); IR (neat) 1368, 1219, 1159, 1088, 1065, 995, 766, and 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ= 1.27 (6H, s), 1.32 (6H, s), 5.98 (1H, s), 7.3—7.4 (3H, m), and 7.4—7.6 (2H, m); MS(EI) *m/z* 206 (M^+; 17), 205 (57), 105 (100), 83 (38), and 77 (41).

4,4,5,5-Tetramethyl-2-(2-nitrophenyl)-1,3-dioxolane (2g). Mp 88—90 °C (from hexane); IR (KBr) 1526, 1356, 1208, 1162, 1102, 1061, 1009, 961, 783, and 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.16 (6H, s), 1.31 (6H, s), 6.50 (1H, s), 7.45 (1H, dt, *J*=7.7 and 1.4 Hz), 7.59 (1H, dt, *J*=7.7 and 1.4 Hz), 7.86 (1H, dd, *J*=7.7 and 1.4 Hz), and 7.89 (1H, dd, *J*=7.7 and 1.4 Hz); MS(EI) *m/z* 250 (M^+-1; 3.1), 234 (62), 150 (21), 134 (100), 104 (47), 83 (70), 79 (33), 77 (27), and 76 (17). Found: C, 62.13; H, 6.81; N, 5.55%. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57%.

4,4,5,5-Tetramethyl-2-(3-nitrophenyl)-1,3-dioxolane (3g). Oil; IR (neat) 1534, 1350, 1219, 1156, 1102, 1011, 806, and 727 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25 (6H, s), 1.34 (6H, s), 6.02 (1H, s), 7.54 (1H, t, *J*=7.9 Hz), 7.82 (1H, dt, *J*=7.9 and 1.3 Hz), 8.18 (1H, ddd, *J*=7.9, 2.1, and 1.3 Hz), and 8.37 (1H, t, *J*=2.1 Hz); MS(EI) *m/z* 251 (M^+; 11), 250 (51), 234 (20), 193 (22), 176 (8.6), 150 (100), 135 (48), 105 (60), 85 (71), 83 (64), 77 (28), and 76 (25). Found: C, 61.85; H, 6.85; N, 5.50%. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57%.

4,4,5,5-Tetramethyl-2-(4-nitrophenyl)-1,3-dioxolane (4g).[25] Mp 89—90 °C (from hexane); IR (KBr) 1524, 1343, 1215, 1152, 1078, 1008, 991, and 729 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.22 (6H, s), 1.33 (6H, s), 6.02 (1H, s), 7.66 (2H, d, *J*=8.8 Hz), and 8.22 (2H, d, *J*=8.8 Hz); MS(EI) *m/z* 251 (M^+; 17), 250 (60), 234 (18), 193 (22), 176 (35), 150 (100), 136 (23), 105 (21), 85 (64), 83 (71), 77 (28), and 76 (15). Found: C, 61.96; H, 6.89; N, 5.60%. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82; N, 5.57%.

2,4,4,5,5-Pentamethyl-2-phenyl-1,3-dioxolane (1h). Bp 121—122 °C (16 mmHg) (lit,[8b] 77—78 °C (1.2 mmHg)); IR (neat) 1370, 1258, 1154, 978, 766, and 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.00 (6H, s), 1.31 (6H, s), 1.59 (3H, s), 7.1—7.3 (3H, m), and 7.4—7.6 (2H, m); MS(EI) *m/z* 205 (M^+-15; 41), 161 (14), 143 (6.3), 105 (100), 83 (48), and 77 (27). Found: C, 76.06; H, 9.39%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

2,4,4,5,5-Pentamethyl-2-(2-nitrophenyl)-1,3-dioxolane (2h). Mp 119—120 °C (from hexane–ethyl acetate); IR (KBr) 1534, 1372, 1150, 1237, 978, 936, 851, 781, 758, and 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (6H, s), 1.24 (6H, s), 1.81 (3H, s), 7.3—7.5 (3H, m), and 7.6—7.7 (1H, m); MS-(EI) *m/z* 250 (M^+-15; 45), 166 (8.6), 150 (100), 101 (19), 91 (30), 85 (15), 83 (52), 77 (13), and 76 (10). Found: C, 63.36; H, 7.23; N, 5.29%. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28%.

2,4,4,5,5-Pentamethyl-2-(3-nitrophenyl)-1,3-dioxolane (3h). Mp 55—56 °C (from hexane); IR (KBr) 1526, 1346, 1250, 1152, 974, and 933 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.99 (6H, s), 1.33 (6H, s), 1.59 (3H, s), 7.43 (1H, t, *J*=7.9 Hz), 7.83 (1H, dt, *J*=7.9 and 1.2 Hz), 8.10 (1H, ddd, *J*=7.9, 2.2, and 1.2 Hz), and 8.38 (1H, t, *J*=2.2 Hz); MS(EI) *m/z* 250 (M^+-15; 45), 190 (1.9), 166 (3.9), 150 (100), 143 (11), 104 (14), 101 (18), 85 (20), 83 (53), 77 (15), and 76 (11). Found: C, 63.24; H, 7.27; N, 5.29%. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28%.

2,4,4,5,5-Pentamethyl-2-(4-nitrophenyl)-1,3-dioxolane (4h). Mp 65—66 °C (from hexane); IR (KBr) 1522, 1346, 1250, 1150, 1076, 972, 958, 934, 860, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.98 (6H, s), 1.32 (6H, s), 1.58 (3H, s), 7.67 (2H, d, *J*=8.9 Hz), and 8.17 (2H, d, *J*=8.9 Hz); MS (FAB) 265.2, 250.2, and 101.3; MS(EI) *m/z* 250 (M^+-15; 48), 190 (16), 166 (3.7), 160 (8.5), 150 (100), 143 (10), 104 (14), 101 (15), 85 (19), 83 (55), 77 (15), and 76 (9.3). Found: C, 63.38; H, 7.28; N, 5.28%. Calcd for $C_{14}H_{19}NO_4$: C, 63.38; H, 7.22; N, 5.28%.

(4*R*,5*R*)-4,5-Bis(methoxycarbonyl)-2-phenyl-1,3-dioxolane (1j).[25] Mp 75—76 °C (from hexane–ethyl acetate); IR (KBr) 1755, 1431, 1238, 1107, 970, 924, and 766 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.83 (3H, s), 3.88 (3H, s), 4.87 (1H, d, *J*=4.0 Hz), 4.99 (1H, d, *J*=4.0 Hz), 6.15 (1H, s), 7.3—7.5 (3H, m), and 7.5—7.7 (2H, m); MS(EI) *m/z* 265 (M^+-1; 8.7), 207 (25), 145 (8.1), 122 (66), 105 (100), 91 (76), 77 (30), and 59 (34). Found: C, 58.54; H, 5.31%. Calcd for $C_{13}H_{14}O_6$: C, 58.64; H, 5.30%.

(4*R*, 5*R*)-4, 5-Bis(methoxycarbonyl)-2-(2-nitrophenyl)-1,3-dioxolane (2j). Oil; IR (neat) 1759, 1534, 1439, 1350, 1211, 1117, 851, and 791 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.74 (3H, s), 3.89 (3H, s), 4.91 (1H, d, *J*=3.7 Hz), 5.01 (1H, d, *J*=3.7 Hz), 6.81 (1H, s), 7.56 (1H, dt, *J*=7.6 and 1.5 Hz), 7.69 (1H, dt, *J*=7.6 and 1.5 Hz), and

7.9—8.1 (2H, m); MS(EI) m/z 310 (M^+-1; 2.1), 294 (32), 264 (27), 252 (41), 166 (17), 150 (20), 135 (100), 121 (33), 105 (97), 91 (25), 79 (46), 77 (46), and 59 (81). Found: C, 50.52; H, 4.12; N, 4.54%. Calcd for $C_{13}H_{13}NO_8$: C, 50.17; H, 4.21; N, 4.50%.

(4*R*, 5*R*)- 4, 5- Bis(methoxycarbonyl)- 2- (3- nitrophenyl)-1,3-dioxolane (3j). Oil; IR (neat) 1761, 1534, 1439, 1354, 1221, 1115, 976, 899, 812, and 739 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.85 (3H, s), 3.90 (3H, s), 4.92 (1H, d, J=3.6 Hz), 5.02 (1H, d, J=3.6 Hz), 6.26 (1H, s), 7.60 (1H, t, J=7.9 Hz), 7.94 (1H, dt, J=7.9 and 1.2 Hz), 8.28 (1H, ddd, J=7.9, 2.1, and 1.2 Hz), and 8.50 (1H, t, J=2.1 Hz); MS(EI) m/z 311 (M^+; 1.6), 310 (8.9), 264 (19), 252 (68), 166 (69), 150 (78), 145 (80), 136 (89), 113 (64), 77 (32), 76 (17), 73 (84), and 59 (100). Found: C, 50.11; H, 4.15; N, 4.71%. Calcd for $C_{13}H_{13}NO_8$: C, 50.17; H, 4.21; N, 4.50%.

(4*R*, 5*R*)- 4, 5- Bis(methoxycarbonyl)- 2- (4- nitrophenyl)-1,3-dioxolane (4j). Oil; IR (neat) 1759, 1526, 1439, 1350, 1219, 1107, 857, and 752 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.82 (3H, s), 3.89 (3H, s), 4.91 (1H, d, J=3.7 Hz), 5.01 (1H, d, J=3.7 Hz), 6.25 (1H, s), 7.78 (2H, d, J=8.8 Hz), and 8.26 (2H, d, J=8.8 Hz); MS(EI) m/z 311 (M^+; 1.3), 310 (8.5), 264 (1.9), 252 (52), 166 (44), 150 (64), 145 (62), 136 (53), 73 (62), and 59 (100). Found: C, 50.40; H, 4.15; N, 4.72%. Calcd for $C_{13}H_{13}NO_8$: C, 50.17; H, 4.21; N, 4.50%.

2-Benzoyloxyethyl Nitrate (7). Oil; IR (neat) 1725, 1638, 1287, 1267, 1123, 1109, and 858 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.5—4.7 (2H, m), 4.7—4.9 (2H, m), 7.4—7.6 (3H, m), and 8.0—8.1 (2H, m); MS(EI) m/z 211 (M^+; 1.2), 105 (75), and 77 (46). Found: C, 51.06; H, 4.31; N, 6.54%. Calcd for $C_9H_9NO_5$: C, 51.19; H, 4.30; N, 6.63%.

3-Benzoyloxy-2,3-dimethylbutan-2-ol (8).[25] Oil; IR (KBr) 3440, 1715, 1289, 1125, 938, and 712 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.31 (6H, s), 1.64 (6H, s), 3.67 (1H, s), 7.4—7.6 (3H, m), and 7.9—8.0 (2H, m); MS(EI) m/z 207 (M^+-15; 0.5), 164 (14), 105 (75), 77 (33), and 59 (100).

1-(Diacetoxymethyl)-2-nitrobenzene (10a). Mp 86—87 °C (from hexane–ethyl acetate) (lit,[26] 87—88 °C); IR (KBr) 1755, 1526, 1352, 1237, 1202, 1017, 793, and 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.15 (6H, s), 7.5—7.7 (2H, m), 8.06 (2H, d), and 8.20 (1H, s); MS(EI) m/z 207 (M^+-46; 0.5), 194 (0.9), 165 (4.3), 151 (5.4), 123 (4.5), 121 (5.9), 104 (2.6), 76 (2.9), 65 (3.5), 51 (5.1), and 43 (100).

1-(Diacetoxymethyl)-3-nitrobenzene (10b). Mp 64—65 °C (from hexane–ethyl acetate) (lit,[21] 64—66 °C); IR (KBr) 1758, 1534, 1352, 1240, 1202, 1011, 992, 820, and 743 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.17 (6H, s), 7.61 (1H, t, J=7.9 Hz), 7.74 (1H, s), 7.84 (1H, dt, J=7.9 and 1.3 Hz), 8.28 (1H, ddd, J=7.9, 2.1, and 1.3 Hz), and 8.41 (1H, t, J=2.1 Hz); MS(EI) m/z 210 (M^+-43; 0.4), 194 (0.6), 150 (5.9), 134 (3.5), 105 (3.4), 77 (5.1), 51 (6.5), and 43 (100).

1-(Diacetoxymethyl)-4-nitrobenzene (10c). Mp 127—128 °C (from hexane–ethyl acetate) (lit,[26] 125 °C); IR (KBr) 1763, 1530, 1350, 1230, 1203, 976, 857, 830, and 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.16 (6H, s), 7.70 (2H, d, J=8.8 Hz), 7.73 (1H, s), and 8.27 (2H, d, J=8.8 Hz); MS (EI) m/z 210 (M^+-43; 0.6), 194 (0.5), 169 (0.3), 150 (5.5), 134 (1.1), 105 (1.4), 77 (3.1), 51 (4.1), and 430 (100).

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