The Oxidation of 1,3-Butadienes with Nitric Acid into 2,5-Dihydrofurans

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The oxidation of 3,4-bis(diphenylmethylene)-succinic anhydride (I), -1-benzylsuccinimide (VI), and -γ-butyrolactone (VIII) with nitric acid afforded the corresponding 2,5-dihydrofuran derivatives, III, VII, and IX respectively. The same oxidation of 3,4-bis(diphenylmethylene)cyclobutane-1,2-dione (XI) afforded 3,4-bis(diphenylhydroxymethyl)cyclobut-3-ene-1,2-dione (XIII), probably *via* the bicyclic cyclobutenedione intermediate (XII).

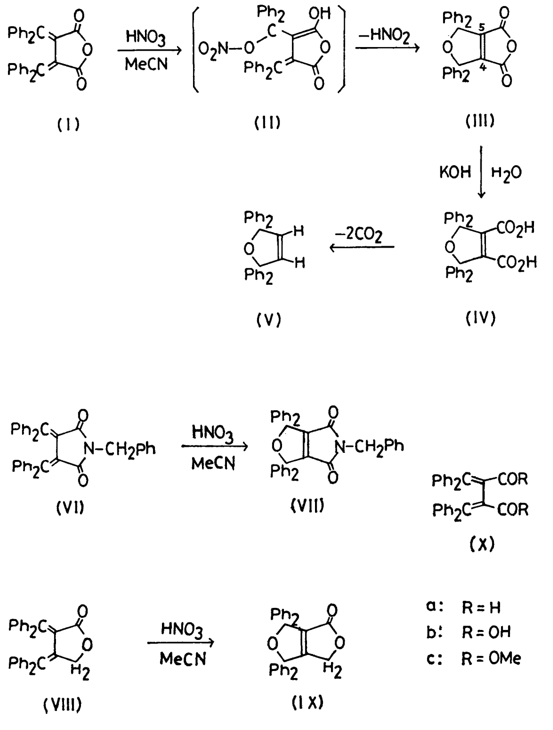
No one-step oxidation of buta-1,3-diene into dihydrofuran has yet been reported. We have now performed the oxidation of the buta-1,3-diene group of I, VI, VIII, and XI with HNO_3 into dihydrofuran.

When a solution of 3,4-bis(diphenylmethylene)succinic anhydride (I)¹⁾ and concd HNO_3 in MeCN was heated under reflux for 10 min, 6,6,8,8-tetraphenyl-2,7-dioxabicyclo[3.3.0]oct-4-ene-1,3-dione (III) was obtained in an 89% yield. The structure of III was identified by the decarboxylation of the 2,2,5,5-tetraphenyl-3,4-dicarboxy-2,5-dihydrofuran (IV) initially produced by the hydrolysis of III; this afforded 2,2,5,5-tetraphenyl-2,5-dihydrofuran (V).²⁾ The same treatment of 3,4-bis(diphenylmethylene)-1-benzylsuccinimide (VI)³⁾ and -γ-lactone (VIII)⁴⁾ afforded 6,6,8,8-tetraphenyl-2-benzyl-2-aza-7-oxabicyclo[3.3.0]oct-4-ene-1,3-dione (VII) (85%) and 6,6,8,8-tetraphenyl-2,7-dioxabicyclo[3.3.0]oct-4-en-1-one (IX) (51%) respectively.

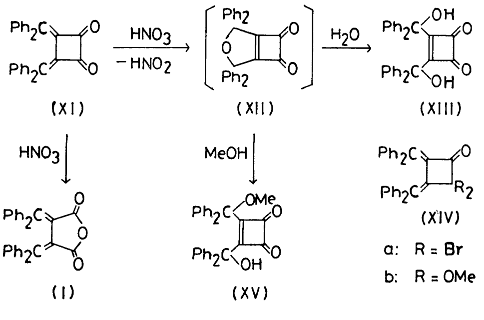
However, 2,3-bis(diphenylmethylene)-butane-1,4-dial (Xa), -succinic acid (Xb), and its dimethyl ester (Xc) were not oxidized with concd HNO_3. This shows that a fixed s-*cis* configuration of the buta-1,3-diene moiety is essential for the oxidation. Since I was not oxidized with concd $HClO_4$, HBF_4, and H_2SO_4, concd HNO_3 may be a characteristic reagent for the oxidation reaction. A possible pathway of the oxidation of I is illustrated in Scheme 1, *i. e.*, the elimination of HNO_2 from the II initially formed by the 1,4-addition of HNO_3 to the enone group of I.

The same treatment of 3,4-bis(diphenylmethylene)-cyclobutane-1,2-dione (XI) with concd HNO_3 in MeCN afforded I and 3,4-bis(diphenylhydroxymethyl)cyclobut-3-ene-1,2-dione (XIII)⁵⁾ in 37 and 17% yields respectively. Since the oxidation of XI with 30% H_2O_2 or with concd $HClO_4$ to afford I has been reported,¹⁾ I may be produced by a similar Baeyer-Villiger-type oxidation of XI. When the reaction of XI with concd HNO_3 was carried out in a non-poalr solvent such as CCl_4, this Baeyer-Villiger oxidation was inhibited, and XIII was obtained in a 64% yield as the sole isolable product. A possible precursor of XIII is the bicyclic cyclobutenedione (XII), which can be produced by the oxidation of XI *via* a pathway similar to that described for the formation of III.

In order to prove the intermediacy of XII, XI was allowed to react with concd HNO_3 in MeOH, in the expectation of isolating 3-diphenylhydroxymethyl-4-diphenylmethoxymethylcyclobut-3-ene-1,2-dione (XV). The reaction, however, afforded only 2,2-dimethoxy-3,4-bis(diphenylmethylene)cyclobutan-1-one (XIVb),¹⁾ no XV. Nevertheless, when MeOH was added to a reaction mixture of XI, concd HNO_3, and CCl_4, soon the green color of XI disappeared and XV was isolated in a 54% yield. Since XIII did not react with MeOH in the presence of concd HNO_3 at an elevated temperature, the possibility that XIII is a precursor of XV can be ruled out. A plausible pathway of the formation of XV is an acid-catalyzed methanolysis of XII (Scheme 2). Unfortunately, however, all attempts to isolate XII failed.



Scheme 1.



Scheme 2.

The reaction of 2,2-dibromo-3,4-bis(diphenylmethylene)cyclobutan-1-one (XIVa) with concd HNO_3 in MeCN for 2 min afforded I in a 52% yield. The same treatment of XIVb as for XIVa for 2 min afforded XI in a 45% yield.

Experimental

All the melting points were uncorrected. The IR, UV, and NMR spectra were measured in Nujol mull, $CHCl_3$, and $CDCl_3$ respectively, unless otherwise noted. The mass spectra were measured with an ionization energy of 75 eV.

Oxidation of I. A solution of I (1.2 g) and concd HNO_3 (0.8 ml) in MeCN (100 ml) was heated under reflux for 10 min. Crude crystals left by the evaporation of the solvent were recrystallized from MeCN to afford III as colorless needles; 1.0 g (89%); mp 196—197 °C. IR: 1850 and 1780 (C=O), 1670 (C=C), and 1020 cm^{-1} (C–O–C); λ_{max}: 264 (ε, 4700) and 280 nm (4700); NMR: 2.78 τ (s, Ph); MS: *m/e* (rel intensity) 444 (M^+, 30), 323 (100), 289 (80), and 218 (55).

Found: C, 79.81; H, 4.68%. Calcd for $C_{30}H_{20}O_4$: C, 81.06; H, 4.54%.

Hydrolysis of III. A solution of III (0.19 g) and KOH (0.2 g) in MeOH (30 ml) was heated under reflux for 2 hr. The crude crystals which had been separated out by the addition of dil HCl to the reaction mixture were recrystallized from MeCN to afford IV as colorless needles; 0.16 g (74%); mp 204—205 °C. IR: 1740 and 1720 (unsplit doublet, C=O), 1650 (C=C), and 1030 cm^{-1} (C–O–C); λ_{max}^{EtOH}: 240 sh (ε, 10500), 258 sh (5100), and 216 sh nm (3700). MS: *m/e* (rel intensity) 323 (100) and 218 (40).

Found: C, 77.69; H, 4.78%. Calcd for $C_{30}H_{22}O_5$: C, 77.91; H, 4.80%.

Decarboxylation of IV. A mixture of IV (0.104 g), Cu-powder (0.05 g) and quinoline (3 ml) was heated under reflux for 4 hr. The cooled reaction mixture was then diluted with ether (100 ml). The ethereal solution was washed successively with dil HCl and water, and then dried over anhydrous Na_2SO_4. The crude crystals left after the evaporation of the solvent were recrystallized from MeCN to afford V as colorless needles; 0.012 g (14%); mp 179—181 °C (lit,[2] mp 180—183 °C). IR: 1010 cm^{-1} (C–O–C); λ_{max}: 250 sh (ε, 900), 253 (1100), 260 (1200), and 266 nm (1000); NMR: 2.82 (s, Ph, 20H) and 3.52 τ (s, =CH, 2H).

Oxidation of VI. VI (0.1 g) was treated with concd HNO_3 (0.08 ml) in MeCN (10 ml) under the same conditions as were used for I. The crude crystals left by the evaporation of the solvent were recrystallized from MeCN to afford VII as colorless needles; 0.087 g (85%); mp 178—179 °C. IR: 1775 and 1715 (C=O), 1435 (CH_2), and 1010 cm^{-1} (C–O–C); λ_{max}: 252 (ε, 14200) and 295 sh nm (5100); NMR: 2.4—3.2 (m, Ph, 25H) and 5.29 τ (s, CH_2, 2H).

Found: C, 83.15; H, 4.83%. Calcd for $C_{37}H_{27}O_3N$: C, 83.28; H, 5.10%.

Oxidation of VIII. VIII (0.1 g) was treated with concd HNO_3 (0.08 ml) in MeCN (10 ml) under the same conditions as were used for I. The crude crystals left after the evaporation of the solvent were recrystallized from MeCN to afford IX as colorless needles; 0.053 g (51%); mp 227—228 °C. IR: 1770 (C=O), 1675 (C=C), and 1010 cm^{-1} (C–O–C); λ_{max}: 260 sh (ε, 4100), 263 sh (3100), and 270 sh nm (1800); NMR: 2.3—3.2 (m, Ph, 20H) and 4.95 τ (s, CH_2, 2H).

Found: C, 83.55; H, 4.95%. Calcd for $C_{30}H_{22}O_3$: C, 83.70; H, 5.15%.

Oxidation of XI in MeCN. XI (0.1 g) was allowed to react with concd HNO_3 (0.05 ml) in MeCN (20 ml) under the same conditions as were used for I. The evaporation of the solvent gave a mixture of red and colorless crystals. The subsequent recrystallization of this mixture from AcOEt afforded I as red rhombs; 0.038 g (37%); mp 230 °C (lit,[1] mp 230 °C). The AcOEt solution left after the separation of I was evaporated to dryness, and the residue was recrystallized from MeOH to afford XIII as colorless prisms; 0.018 g (17%); mp 205—206 °C (lit,[5] mp 205—206 °C). The IR spectra of I and XIII were identical with those of the authentic samples.

Oxidation of XI in CCl_4. XI (0.1 g) was oxidized with concd HNO_3 (0.05 ml) in CCl_4 (20 ml) by the procedure used for MeCN. The crude crystals left by the evaporation of the solvent were recrystallized from MeOH to afford XIII; 0.069 g (64%).

Oxidation of XI in CCl_4. XI (0.1 g) was oxidized with concd HNO_3 (0.05 ml) in CCl_4 (20 ml) by the procedure used for MeCN. The crude crystals left by the evaporation of the solvent were recrystallized from MeOH to afford XIII; 0.069 g (64%).

Isolation of XV. A solution of XI (0.1 g) and concd HNO_3 (0.07 ml) in CCl_4 (20 ml) was heated under reflux until the green color of XI almost disappeared (*ca.* 7 min). MeOH (10 ml) was then immediately added to the reaction mixture, and it was heated under reflux for 5 min. The crude crystals left by the evaporation of the solvent were recrystallized from MeOH to afford XV as colorless needles; 0.06 g (54%); mp 138—140 °C. IR: 3580 and 3300 (OH), 1790 sh and 1780 (C=O), 1560 (C=C), and 1070 cm^{-1} (C–O–C); λ_{max}^{EtOH}: 241 sh (ε, 13500) and 274 sh nm (6500); NMR: 2.70 (s, Ph, 20H), 3.22 (s, OH, 1H), and 7.04 τ (s, OCH_3, 3H).

Reaction of XI with Concd HNO_3 in MeOH, A solution of XI (0.1 g) and concd HNO_3 (0.07 ml) in MeOH (20 ml) heated under reflux for 2 hr. The crude crystals left by the evaporation of the solvent were recrystallized from AcOEt to afford XIVb as orange red needles; 0.074 g (67%); mp 191—192 °C (lit,[1] mp 191—192 °C). The IR spectrum was identical with that previously-recorded for XIVb.[1]

Reaction of XIVa with Concd HNO_3. A solution of XIVa (0.1 g) and concd HNO_3 (0.04 ml) in MeCN (15 ml) was heated under reflux for 2 min. The crude crystals left by the evaporation of the solvent were recrystallized from AcOEt to afford I as red rhombs; 0.04 g (52%).

Reaction of XIVb with Concd HNO_3. When XIVb (0.1 g) was treated with concd HNO_3 (0.04 ml) in MeCN (15 ml) for 2 min by the procedure used for XIVa, XI was obtained as green prisms; 0.04 g (45%); mp 206—207 °C (lit,[1] mp 206—207 °C). The IR spectrum was identical with that previously-recorded for XI.[1]

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