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Acid-induced Ring-opening of 2′-Substituted Spiro[anthracene-9(10H), 1′-cyclopropan]-10-ones

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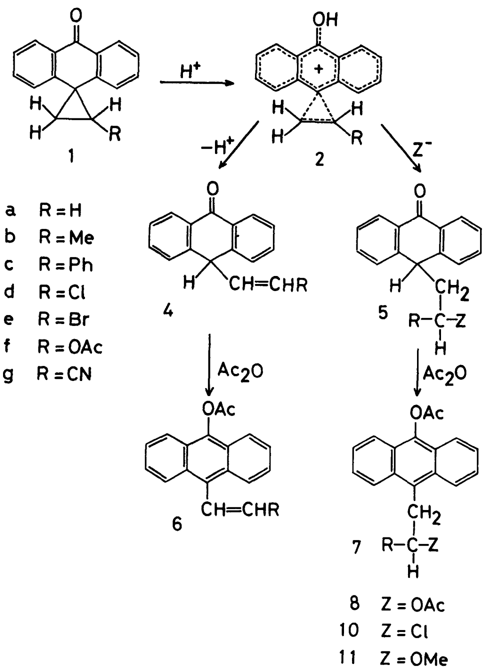
Synopsis. The title compounds (**1**) reacted under acidic conditions to give cyclopropane ring-opened products. In these reactions of **1** bearing methyl-, phenyl-, chloro-, bromo-, and acetoxy-substituents, the cyclopropane ring opened from the more substituted side.

We have previously investigated the reactions of spiro keto compounds.[1,2] In these investigations, it has been found that phenyl-substituted spiro[anthracene-9(10*H*),1′-cyclopropan]-10-ones undergo thermal rearrangement with ring expansion to aceanthrylen-6(2*H*)-ones, whereas a simple cyclopropane-opening, involving the formation of the hydroxy-carbonium ion (*e.g.* **2**) as an intermediate, is observed in the acid-induced reaction. We have further examined the cyclopropane-opening reactions of 2′-substituted spiro[anthracene-9(10*H*),1′-cyclopropan]-10-ones **1** under acidic conditions and their utilization in the preparations of substituted anthracenes.



Results and Discussion

The spiro anthrones **1a**—**c** and **g** were prepared by previously known procedures.[3] The spiro anthrones **1d**—**f** were obtained in 66, 45, and 53% yields, respectively, by irradiation of 10-diazoanthrone (**3**) in the presence of an appropriate olefin.

As was observed in the previous work, the expected products **4** and **5** in the reaction with acidic reagent (HZ) were too unstable to be isolated.[1] Therefore, the acid-induced reactions were carried out in acetic anhydride in the presence of a small amount of mineral acid to convert **4** and **5** to isolable **6** and **7**. Treatment of **1a**, **b**, and **f** with acetic anhydride–sulfuric acid gave **8a** (86%), **b** (81%), and **f** (33%), respectively.[4] The structures of products were assigned as **8** rather than $AcOC_{14}H_8CHRCH_2OAc$, cyclopropane ring-opening from the less substituted side, by their ^1H NMR spectral data: *e.g.* the assignment of **8b** is based on its absorption for methylene and methine hydrogens at δ 3.74 (center, m) and 5.27 (m), respectively; these values are normal compared with those estimated from the absorption which was found in **8a**. The structure $AcOC_{14}H_8$-$CHMeCH_2OAc$ should exhibit methylene absorption near δ 4.12—4.56 (for CH_2CH_2OAc of **8a**), and the observed methine absorption at δ 5.27 is too far downfield to support this claim. The similar acid-induced reactions of 2′-halogenosubstituted spiro anthrones **1d** and **e** afforded 10-acetoxy-9-(formylmethyl)anthracene (**9**) (14—17%) and **8f** (34—35%). The anthracene **9** was identified on the basis of its spectral data and chemical behavior, *i.e.* the reaction of **9** with acetic anhydride in the presence of sulfuric acid led to **8f**. The formation of **9** may be accounted for by the formation of the anthracenes **7d** and **e** followed by elimination of acyl halide.[5] On the other hand, the reaction of **1g** bearing such strongly electron-withdrawing groups as CN gave a complex mixture.

The reactions of **1a**, **b**, **d**, and **e** with acetic anhydride-hydrochloric acid yielded **10a** (78%), **b** (75%), **d** (71%), and **e** (69%), respectively, as the major products, together with **8a** (4%), **b** (5%), **9** (10%), and **9** (9%), respectively, as the minor products. The structural assignments of **10** are based on their ^1H NMR spectral data. The predominant formation of **10** is compatible with the common observation that a chloride ion is more nucleophilic than an acetate ion.[6] Under similar conditions, the spiro anthrones **1c** and **f** afforded a complex product mixture, and **1g** gave no products.

The ring-opening of **1** with hydrochloric acid in methanol were further examined. As mentioned above, the products of the type **5** (Z=Cl or OMe) were too unstable to be isolated, so that they were isolated after acetylation. The reactions of **1a** and **b** gave **10a** (70%) and **b** (65%), respectively. In the similar treatment of **1c**, the anthracene **11c**, which resulted from the solvolysis of **5c** (Z=Cl) in methanol, was obtained in a 69% yield. The similar treatment of **1d**, **e**, and **g** with methanolic hydrochloric acid gave no product.

The spiro anthrone system is intriguing in that the protonation of the carbonyl oxygen may lead to a hydroxy-carbonium ion **2** which is conceivably bridged.[7] The direction of the cyclopropane-opening is consistent with the expectation that the relative stability of the incipient cationic centers will be a controlling factor.

Experimental

*Preparations of 2′-Substituted Spiro[anthracene-9(10*H*),1′-cyclopropan]-10-ones **1**.* ***1d***: A solution of 10-diazoanthrone (**3**)[8] (3.30 g, 15 mmol) in benzene (300 ml) was saturated with vinyl chloride, and the resulting mixture was then irradiated at 5 °C with a 100 W high pressure mercury lamp through a Pyrex filter until TLC showed the absence of **3** (*ca.* 12 h). The solvent and unchanged vinyl chloride were removed under reduced pressure; then the residue was chromatographed on silica gel (benzene as eluant). The first eluate gave **1d** as colorless needles (2.52 g, 66%), mp 122—123 °C.

1e: The product from photoreaction of **3** (3.30 g, 15 mmol) with vinyl bromide (32.1 g, 0.3 mol) in benzene (300 ml) under nitrogen was chromatographed to give **1e** as colorless needles (2.02 g, 45%), mp 134—135 °C.

1f: A similar photoreaction of **3** (3.30 g, 15 mmol) and vinyl acetate (28.8 g, 0.3 mol) in benzene (300 ml) gave **1f** as colorless microcrystals (2.21 g, 53%), mp 94—95 °C.

The spectral and analytical data of **1d**—**f** are consistent with the proposed structures.

*Reaction of **1** with Acetic Anhydride–Sulfuric Acid.* A solution of a spiro anthrone **1** (2—3 mmol) in acetic anhydride (30 ml) containing sulfuric acid (0.5 ml) was allowed to stand at room temperature (10 h). After TLC showed the absence of the starting material, the mixture was poured into water. The precipitate was worked up by recrystallization or chromatography. Spectral and analytical data of the products are given below.

8a: Yellow needles (from benzene); mp 157 °C; IR (KBr disc) 1768 and 1750 cm^{-1} (CO); ^{1}H NMR ($CDCl_3$) δ 2.20 (3H, s), 2.51 (3H, s), 3.58—4.02 (2H, a part of A_2B_2), 4.12—4.56 (2H, a part of A_2B_2), and 7.15—8.95 (8H, m); MS *m/e* 332 (M$^+$). Found: C, 74.60; H, 5.68%. Calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63%.

8b: Yellow microcrystals (from benzene–hexane); mp 130—131 °C; IR 1778 and 1746 cm^{-1} (CO); ^{1}H NMR δ 1.13 (3H, d, J=6.5 Hz), 1.93 (3H, s), 2.50 (3H, s), 3.63 and 3.84 (1H each, AB part of ABX, J_{AB}=13.5, J_{AX}=8,2, J_{BX}=5.7 Hz), 5.27 (1H, m), and 7.25—8.58 (8H, m); MS *m/e* 336 (M$^+$). Found: C, 74.94; H, 6.00%. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99%.

8f: Yellow microcrystals (from benzene–hexane); mp 185—186 °C; IR 1760 cm^{-1} (CO); ^{1}H NMR δ 1.90 (6H, s), 2.62 (3H, s), 4.10 (2H, d, J=6.0 Hz), 7.12 (1H, t, J=6.0 Hz), and 7.40—8.65 (8H, m); MS *m/e* 380 (M$^+$). Found: C, 69.33; H, 5.38%. Calcd for $C_{22}H_{20}O_6$: C, 69.46; H, 5.30%.

9: Yellow microcrystals (from benzene); mp 198—200 °C; IR 1755 and 1726 cm^{-1} (CO); ^{1}H NMR δ 2.66 (3H, s), 4.65 2H, d, J=2.1 Hz), 7.35—8.35 (8H, m), and 9.83 (1H, t, J=2.1 Hz); MS *m/e* 278 (M$^+$). Found: C, 77.51; H, 5.12% Calcd for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07%.

*Reactions of **1** with Acetic Anhydride–Hydrochloric Acid.* The procedure was identical with that described above, except that hydrochloric acid (1 ml) was used instead of sulfuric acid. The products were isolated by chromatography, followed by recrystallization from benzene–hexane. The characterization data of products are given below.

10a: Pale yellow needles; mp 206—207 °C; IR 1765 cm^{-1} (CO); ^{1}H NMR δ 2.58 (3H, s), 3.52—4.22 (4H, m), and 7.25—8.40 (8H, m); MS *m/e* 300/298 (M$^+$). Found: C, 72.46; H, 5.10; Cl, 11.76%. Calcd for $C_{18}H_{15}O_2Cl$: C, 72.35; H, 5.06; Cl, 11.87%.

10b: Pale yellow needles; mp 173 °C; IR 1768 cm^{-1} (CO); ^{1}H NMR δ 1.44 (3H, d, J=6.5 Hz), 2.55 (3H, s), 3.64—4.78 (3H, m), and 7.25—8.42 (8H, m); MS *m/e* 314/312 (M$^+$). Found: C, 72.85; H, 5.61; Cl, 11.22%. Calcd for $C_{19}H_{17}O_2Cl$: C, 72.96; H, 5.48; Cl, 11.33%.

10d: Pale yellow needles; mp 192—193 °C.

10e: Yellow needles; mp 195—196 °C.

*Reactions of **1** with Methanol–Hydrochloric Acid.* A solution of **1** (2—3 mmol) in methanol containing hydrochloric acid (1 ml) was refluxed under nitrogen for 1 h. The solvent was removed under reduced pressure. After the usual acetylation using acetic anhydride, the products were purified by recrystallization or chromatography.

11c: Yellow needles (from benzene–hexane); mp 160 °C; IR 1755 cm^{-1} (CO); ^{1}H NMR δ 2.56 (3H, s), 3.06 (3H, s), 3.55—4.65 (3H, m), and 7.15—8.35 (8H, m); MS *m/e* 370 (M$^+$). Found: C, 81.05; H, 5.95%. Calcd for $C_{25}H_{22}O_3$: C, 81.05; H, 5.99%.

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