Effects of Substituents on the Formation of Acetals of 4-Substituted 1,3-Indandiones

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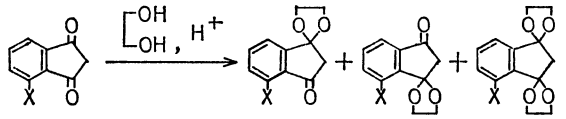
Treatment of 4-nitro-1,3-indandione (**1**) with an equivalent of ethylene glycol in benzene in the presence of *p*-toluenesulfonic acid afforded 4-nitro-1,3-indandione-1-ethylene acetal (**2**), 3-ethylene acetal (**3**) and 1,3-bis-ethylene acetal (**4**). Kinetic studies revealed that **2** is a kinetically preferred product and **3** is a thermodynamically preferred product. However, the reaction of 4-acetamido-1,3-indandione (**5**) with ethylene glycol under similar conditions gave 4-acetamido-1,3-indandione-1-ethylene acetal (**6**) as a product both kinetically and thermodynamically controlled. Thioacetalization of **1** with an equivalent of 1,2-ethanedithiol afforded selectively 4-nitro-1,3-indandione-1-ethylene thioacetal (**9**).

The regioselective preparation of an acetal of polycarbonyl compounds is in general difficult.[1] From the need of monoacetals of 4-substituted 1,3-indandiones for our synthetic studies of azaacenaphthene derivatives, we studied the acetalization of 4-substituted 1,3-indandiones and found that the keto groups, where the acetalization takes place, are largely influenced by the substituents attached and alcohols used. The results are summarized and the mechanisms of the reactions are discussed in the present paper.

Results and Discussion

Reactions and Mechanisms. Treatment of 4-nitro-1,3-indandione (**1**) with an equivalent of ethylene glycol in benzene in the presence of *p*-toluenesulfonic acid afforded a mixture of 4-nitro-1,3-indandione-1-ethylene acetal (**2**), 4-nitro-1,3-indandione-3-ethylene acetal (**3**) and 4-nitro-1,3-indandione-1,3-bisethylene acetal (**4**). The reaction of **1** with a large excess of ethylene glycol under similar conditions gave only **4**. Products **2**, **3** and **4** were isolated by repeated fractional recrystallization.



1; X=NO2 2; X=NO2 3; X=NO2 4; X= NO2

5; X=NHAc 6; X=NHAc 7; X=NHAc 8; X= NHAc

The yields of **2**, **3** and **4** varied with reaction time when the reaction of **1** with an equivalent of ethylene glycol was carried out in benzene in the presence of *p*-toluenesulfonic acid. The yields of **2**, **3** and **4** were determined by vpc analysis of the reaction mixture at appropriate time intervals.[2] The results are shown in Fig. 1. At an initial stage of the reaction, the yield of **2** was higher than that of **3**. Aftre a while, however, the situation was reversed and finally the yields of **2**, **3** and **4** approached constant values.

When **2** was refluxed in benzene in the presence of *p*-toluenesulfonic acid without ethylene glycol, **3** and **4** were obtained. A similar treatment of **3** yielded **2** and **4**. Variation of the yields of the products with reaction time for these reactions were followed by vpc analyses of the reaction mixtures. The results are shown in Figs. 2 and 3. The results indicate that the rate of disappearance of **2** is greater than that of **3**, and that **3** and **4** are produced from **2** at almost equal rates. The rates of formation of **2** and **4** from **3** are also almost equal.

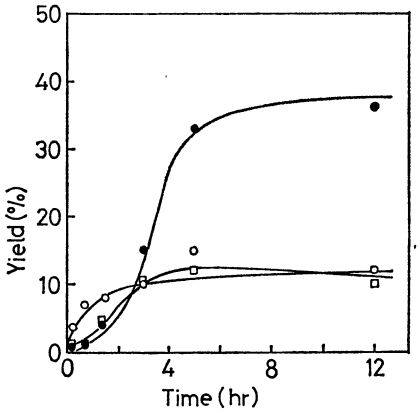


Fig. 1. Variation of the yields of the products with reaction time in the acid-catalyzed acetalization of **1** with ethylene glycol. A mixture of 5.7 g (0.03 mol) of **1**, 1.8 g (0.03 mol) of ethylene glycol and 0.3 g of *p*-TsOH·H_2O in 300 ml of benzene was refluxed. ○: **2**, ●: **3**, □: **4**.

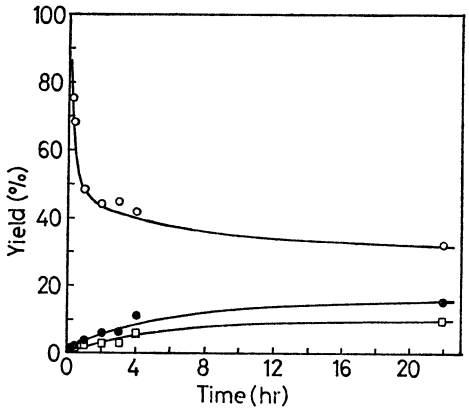


Fig. 2. Variation of the yields of the products with reaction time in the acid-catalyzed reaction of **2**. A mixture of 12.2 mg (0.052 mmol) of **2** and 1.0 mg of *p*-TsOH·H_2O in 1.0 ml of benzene was refluxed. ○: **2**, ●: **3**, □: **4**.

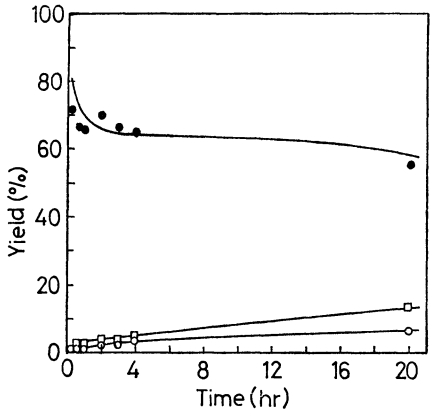
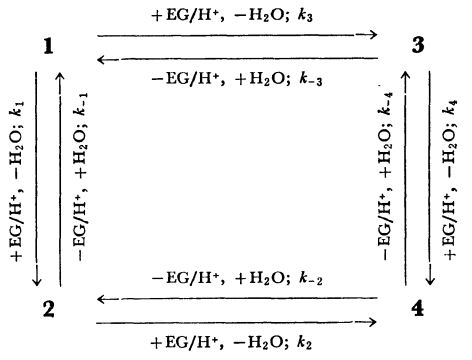


Fig. 3. Variation of the yields of the products with reaction time in the acid-catalyzed reaction of **3**. A mixture of 11.1 mg (0.047 mmol) of **3** and 1.0 mg of *p*-TsOH·H_2O in 1.0 ml of benzene was refluxed.
○: **2**, ●: **3**, □: **4**.

The results may be accounted for by assuming that the acid-catalyzed acetalization of **1** with ethylene glycol proceeds through the pathways represented in Scheme 1.[3] Since $k_1 > k_3$, the formation of **2** is favored over that of **3** at the initial stage of acetalization.



Scheme 1.

However, as a result of $k_{-1} > k_{-3}$ the yield of **3** becomes higher than that of **2** after a prolonged reaction, indicating that **3** is a thermodynamically controlled product; **3** is thermodynamically more stable than **2**.

As another example of acetalization, we studied the acid-catalyzed acetalization of 4-acetamido-1,3-indandione (**5**) with ethylene glycol. Treatment of **5** with an equivalent of ethylene glycol in benzene in the presence of *p*-toluenesulfonic acid gave 4-acetamido-1,3-indandione-1-ethylene acetal (**6**), accompanied by a black material which could not be purified. In this reaction, 3-ethylene acetal (**7**) and 1,3-bisethylene acetal (**8**) were not detected. Variation of the yield of **6** with reaction time is shown in Fig. 4. Treatment of **7** in benzene in the presence of *p*-toluenesulfonic acid afforded **5** and **6**. Variation of the yields of **5** and **6** with reaction time is shown in Fig. 5. The results suggest that **6** is a product which is both kinetically and thermodynamically preferable in the acetalization of **5**. The results also indicate that the acetal formation of 1,3-indandiones is strongly influenced by the substituents attached to the benzene ring in the diones; an

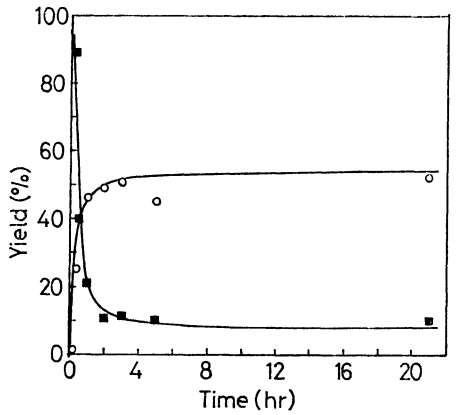


Fig. 4. Variation of the yields of the products with reaction time in the acid-catalyzed acetalization of **5**. A mixture of 50.9 mg (0.25 mmol) of **5**, 35.3 mg (0.57 mmol) of ethylene glycol and 5.3 mg of *p*-TsOH·H_2O in 5.0 ml of benzene was refluxed.
■: **5**, ○: **6**.

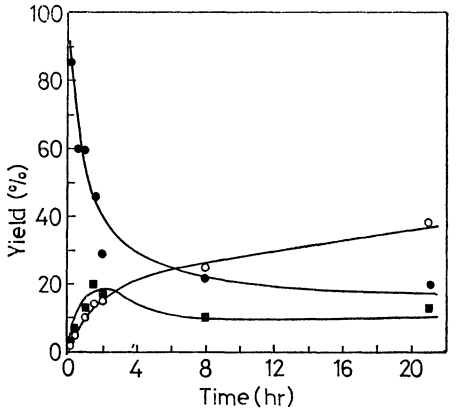
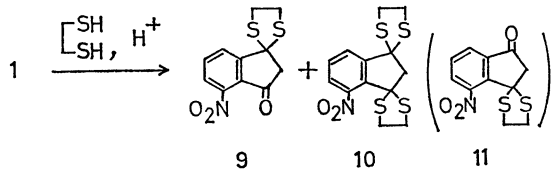


Fig. 5. Variation of the yields of the products with reaction time in the acid-catalyzed reaction of **7**. A mixture of 9.9 mg (0.04 mmol) of **7** and 1.0 mmg of *p*-TsOH·H_2O in 1.0 ml of benzene was refluxed.
■: **5**, ○: **6**, ●: **7**.

electron-withdrawing substituent such as a nitro group at the 4-position stabilizes 3-ethylene acetal, but an electron-releasing substituent at the same position stabilizes 1-ethylene acetal.[4] However, it must be borne in mind that in a kinetical sense, the carbonyl group at the 1-position is more reactive than the carbonyl group at the 3-position, irrespective of the nature of substituents.[5]

In contrast to ethylene acetals, ethylene thioacetals are relatively stable under the conditions of their formation; they are not easily hydrolyzed by mineral acids. Consequently, in the case of thioacetals, a predominant formation of the kinetically controlled products is to be expected: *i.e.*, thioacetalization of **1** would yield selectively 4-nitro-1,3-indandione-1-ethylene thioacetal (**9**). The reaction of **1** with an equivalent of 1,2-ethanedithiol in acetic acid in the presence of *p*-toluenesulfonic acid gave **9** in a 36% yield along with a small amount (1% yield) of 4-nitro-1,3-indandione-1,3-bisethylene thioacetal (**10**), but no 3-ethylene thioacetal (**11**). The reaction of **1** with a large excess

of 1,2-ethanedithiol gave only **10**. A high regioselectivity of this reaction may in part be attributed to a bulkiness of sulfur atoms besides an inherent high reactivity of the carbonyl group at the 1-position.



9 10 11

Characterization of the Products. The structures of the products were established by the sepctral properties and chemical modifications whereby the products can be interrelated. The relevant IR and NMR spectral data of compounds **1**—**9** and 4-acetamido-1,3-indandione-1-ethylene thioacetal (**12**) are listed in Table 1.

The 4-acetamido derivatives **5**, **7** and **8** were prepared respectively from the corresponding 4-nitro derivatives, **1**, **3** and **4**. Catalytic reduction of **1**, **3** and **4** over a Raney nickel to the corresponding amino derivatives followed by acetylation led to the formation of **5**, **7** and **8**, respectively. Compound **6** was obtained by the acetalization of **5**. The catalytic reduction of **9** over a Raney nickel gave 4-amino-1,3-indandione-1-ethylene thioacetal which was acetylated to yield **12**.

Let us compare the spectral properties of the 4-nitro derivatives with those of the corresponding 4-acetamido derivatives. The carbonyl band in the IR spectrum of 4-nitro-1-ethylene acetal **2** appeared at higher wavenumber than that of 4-acetamido-1-ethylene acetal **6** by 50 cm^{-1}. A similar shift of the carbonyl band was observed in a comparison of 4-nitro-1-ethylene thioacetal **9** with 4-acetamido-1-ethylene thioacetal **12**; *i.e.*, the carbonyl band of **9** appeared at higher wavenumber than that of **12** by 32 cm^{-1}. In contrast, the carbonyl band of 4-nitro-3-ethylene acetal **3** appeared at a wave number almost the same as that of 4-acetamido-3-ethylene acetal **7**.

Another difference in spectral properties between the 1-ethylene acetal (or the 1-ethylene thioacetal) and the 3-ethylene acetal was observed in the NMR spectra. For 1-ethylene acetal **6** and 1-ethylene thioacetal **12**, the signal due to the NH proton appeared at δ 10—11 ppm. On the other hand, the same signals appeared at higher fields, *i.e.*, δ 8—9 ppm, for 3-ethylene acetal **7** and 1,3-bisethylene acetal **8**. All these spectral properties can be interpreted by assuming that an intramolecular interaction exists between the NH and carbonyl groups in 4-acetamido-1-ethylene acetals and 4-acetamido-1-ethylene thioacetal.

Table 1. Spectral properties

Compd	νC=O (cm^{-1})	Compd	νC=O	NH (ppm)
1	1740 1710	**5**	1740 1705	10.08— 10.40
2	1740	**6**	1690	10.07— 10.70
3	1725	**7**	1722	8.03— 8.31
4	—	**8**	—	8.25— 8.90
9	1730	**12**	1698	10.14— 10.54

The chemistry and spectral properties described above are consistent with the assigned structures. Further evidence for the structure assignment was provided by the fact that 5-azaacenaphthene derivatives were synthesized from **2** and **9**.[6]

Experimental

Vpc analyses were carried out on a 063 Hitachi gas chromatograph with a column packed with 30% Silicone-grease on Celite 545 and tlc analyses with Wakogel B5.

4-Nitro-1,3-indandione-1-ethylene Acetal (2). A mixture of 1.9 g (0.01 mol) of 4-nitro-1,3-indandione (**1**),[7] 5.0 g (0.08 mol) of ethylene glycol and 0.1 g of *p*-toluenesulfonic acid monohydrate (*p*-TsOH·H_2O) in 75 ml of benzene was heated under reflux in a Dean-Stark trap for 2 hr, water formed during the reaction being continuously removed. The reaction mixture was then washed with two 20 ml portions of 5% Na_2CO_3. The aqueous layer was extracted with two 30 ml portions of benzene. All the benzene solutions were combined, washed twice with 100 ml of water, dried (Na_2SO_4) and then evaporated. The oily residue was recrystallized from $CHCl_3$–CCl_4 to yield 0.55 g (23%) of the crude **2**. Repeated fractional recrystallization from $CHCl_3$–CCl_4 gave an analytical sample of **2** as white crystals, mp 142—143 °C. IR (KBr): 1740 (C=O), 1539 (NO_2), and 1361 cm^{-1} (NO_2). NMR ($CDCl_3$): δ 3.04 (s, 2H, $-CO-CH_2C(O-)_2$), 4.12—4.50 (m, 4H, $-OCH_2CH_2O-$), and 7.92 ppm (s, 3H, aromatic H); Mass: *m/e* 235 (M^+), 219, 205, 192, 177, 161, 147, and 133.

Found: C, 56.22; H, 3.78; N, 5.88%. Calcd for $C_{11}H_9NO_5$: C, 56.17; H, 3.86; N, 5.96%.

4-Nitro-1,3-indandione-3-ethylene Acetal (3). A mixture of 5.7 g (0.03 mol) of **1**, 1.8 g (0.03 mol) of ethylene glycol and 0.3 g of *p*-TsOH·H_2O in 240 ml of benzene was heated under reflux in a Dean-Stark trap for 24 hr. The reaction mixture was worked up as described above. From the benzene solution, 5.3 g (76%) of crude **3** was obtained. Repeated fractional recrystallization from ethanol gave an analytical sample of **3** as white crystals, mp 134—136 °C. IR(KBr): 1725 (C=O), 1540 and 1362 cm^{-1} (NO_2). NMR ($CDCl_3$): δ 2.95 (s, 2H, $-COCH_2C(O-)_2$), 4.00—4.50 (m, 4H, $-OCH_2-CH_2O-$), and 7.52—8.30 ppm (m, 2H, aromatic H). Mass: *m/e* 235 (M^+), 207, 192, 175, 167, 161, 159, 149, 147, 145, 133, and 113.

Found: C, 55.98; H, 3.70; N, 5.92%. Calcd for $C_{11}H_9NO_5$: C, 56.17; H, 3.86; N, 5.96%.

Upon acidification of the Na_2CO_3 solution, 0.95 g (17%) of crude **1** was recovered.

4-Nitro-1,3-indandione-1,3-bisethylene Acetal (4). A mixture of 5.7 g (0.03 mol) of **1**, 7.2 g (0.12 mol) of ethylene glycol and 0.3 g of *p*-TsOH·H_2O in 200 ml of benzene was heated under reflux in a Dean-Stark trap for 48 hr. The reaction mixture was worked up as described above. Recrystallization of the residue obtained after evaporation of benzene from CCl_4–hexane gave 5.7 g (69%) of **4** as light pink crystals; mp 78—80 °C. IR (KBr): 1535 cm^{-1} (NO_2), no absorption appearing at the carbonyl region. NMR ($CDCl_3$): δ 2.49 (s, 2H, $(-O)_2CCH_2C(O-)_2$), 3.94—4.50 (m, 8H, two of

$-OCH_2CH_2O-$), 7.38—7.64 (m, 2H, aromatic H), and 7.75 ppm (dd, J=6.4 and 3.0 Hz, 1H, aromatic H). Mass: *m/e* 279 (M^+), 262, 249, 233, 207, 191, 177, 162, 161, 147 and 133.

Found: C, 55.95; H, 4.46; N, 4.89%. Calcd for $C_{13}H_{13}NO_6$: C, 55.91; H, 4.70; N, 5.02%.

4-Amino-1,3-indandione. A suspension of 3.8 g (0.02 mol) of **1** and *ca.* 10 g of a W-1 Raney nickel in 340 ml of ethanol was hydrogenated under atmospheric pressure at room temperature for 8 hr. The catalyst was separated and washed thoroughly with ethanol. The filtrate was evaporated to give a deep yellow solid. Recrystallization of the solid from ethanol gave 1.0 g (30%) of the amino compound as yellow needles; mp 203—205 °C. IR (KBr): 3455, 3340 (NH_2), 1720, 1685 (C=O), and 1620 cm^{-1}.

Found: C, 67.27; H, 4.30; N, 8.67%. Calcd for $C_9H_7NO_2$: C, 67.07; H, 4.38; N, 8.69%.

*4-Acetamido-1,3-indandione (**5**).* A solution of 100 mg (0.62 mmol) of 4-amino-1,3-indandione in 2 ml of acetic anhydride was heated at 80 °C for a few minutes. Evaporation of the solvent gave a dark brown oil. Recrystallization of the oil from CCl_4 gave 60 mg (55%) of **5** as yellow plates; mp 120—124 °C. IR (KBr): 3310 (NH), 1740, 1705, 1690 (C=O), and 1600 cm^{-1}. NMR ($CDCl_3$): δ 2.29 (s, 3H, $-COCH_3$), 3.28 (s, 2H, $-COCH_2CO-$), 7.58 (dd, J=7.2 and 1.7 Hz, 1H, aromatic H), 7.80 (t, J=7.2 Hz, 1H, aromatic H), 8.91 (dd, J=7.2 and 1.7 Hz, 1H, aromatic H), and 10.08—10.40 ppm (m, 1H, NH). Mass: *m/e* 203 (M^+), 161, 133, 87, and 43.

Found: C, 65.15; H, 4.22; N, 6.83%. Calcd for $C_{11}H_9NO_3$: C, 65.02; H, 4.46; N, 6.89%.

*4-Acetamido-1,3-indandione-1-ethylene Acetal (**6**).* A mixture of 0.5 g (2.5 mmol) of **5**, 0.6 g (8.1 mmol) of ethylene glycol, and 30 mg of *p*-TsOH·H_2O in 50 ml of benzene was heated under reflux in a Dean-Stark trap for 10 hr. The reaction mixture was worked up by a method similar to that for **2**. Recrystallization of the product from CCl_4-hexane gave 0.1 g (16%) of **6** as yellow crystals; mp 145—147 °C. IR(KBr): 3310 (NH), 1690 (C=O), 1610, and 1540 cm^{-1}. NMR ($CDCl_3$): δ 2.23 (s, 3H, $-COCH_3$), 2.97 (s, 2H, $-COCH_2C<^{O-}_{O-}$), 4.15—4.40 (m, 4H, $-OCH_2CH_2O-$), 7.25 (d, J=7.7 Hz, 1H, aromatic H), 7.65 (t, J=7.7 Hz, 1H, aromatic H), and 8.58 ppm (d, J=7.7 Hz, 1H, aromatic H). Mass: *m/e* 247 (M^+), 205, 177, 162, 149, 133, and 120.

Found: C, 62.85; H, 5.11; N, 5.87%. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.67%.

4-Amino-1,3-indandione-3-ethylene Acetal. A suspension of 2.35 g (0.01 mol) of **3** was hydrogenated on a W-1 Raney nickel in 100 ml of dioxane over 3 hr. The crude product was recrystallized from $CHCl_3$–hexane to give yellow needles; mp 132—135 °C. IR(KBr): 3440, 3350 (NH_2), 1705 (C=O), and 1620 cm^{-1}. NMR($CDCl_3$): δ 2.79 (s, 2H, $-COCH_2C<^{O-}_{O-}$), 3.90—4.62 (m, 4H, $-OCH_2CH_2O-$), 6.77 (dd, J=6.9 and 2.1 Hz, 1H, aromatic H), and 6.91—7.42 ppm (m, 2H, aromatic H).

Found: C, 64.65; H, 5.50; N, 7.02%. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83%.

*4-Acetamido-1,3-indandione-3-ethylene Acetal (**7**).* A solution of 410 mg (2.0 mmol) of 4-amino-1,3-indandione-3-ethylene acetal in 10 ml of dry tetrahydrofuran (THF) was added to a stirred mixture of 300 mg (3.8 mmol) of acetyl chloride and 5 ml of pyridine in 5 ml of dry THF under cooling in an ice-water bath. The mixture was stirred at room temperature for 0.5 hr and then poured into 100 ml of water. The aqueous mixture was extracted with three 200 ml portions of CH_2Cl_2. The extract was washed with two 30 ml portions of water, dried over Na_2SO_4 and evaporated. Recrystallization of the solid from ethanol gave **7** as white needles quantitatively; mp 162—165 °C. IR(KBr) 3345 (NH), 1722, 1690 (C=O), and 1600 cm^{-1}. NMR ($CDCl_3$): δ 2.17 (s, 3H, $-COCH_3$), 2.83 (s, 2H, $-COCH_2C<^{O-}_{O-}$), 4.07—4.41 (m, 4H, $-OCH_2CH_2O-$), 7.42—7.61 (m, 2H, aromatic H), 8.00—8.30 (m, 1H, NH), and 8.69 ppm (dd, J=5.8 and 2.9 Hz, 1H, aromatic H). Mass: *m/e* 247 (M^+), 204, 188, 174, 162, 161, 149, 133, and 120.

Found: C, 62.98; H, 5.19; N, 5.58%. Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.67%.

4-Amino-1,3-indandione-1,3-bisethylene Acetal. A suspension of 2.8 g (0.01 mmol) of **4** was hydrogenated on a W-1 Raney nickel in 100 ml of dioxane over 7 hr. Recrystallization of the crude product from CCl_4–hexane gave 2.5 g (quantitative) of the amino compound as yellow needles; mp 132—134 °C. IR(KBr) 3100—3600 (NH_2) and 1620 cm^{-1}.

Found: C, 62.88; H, 5.82; N, 5.90%. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62%.

*4-Acetamido-1,3-indandione-1,3-bisethylene Acetal (**8**).* Acetylation of 4-amino-1,3-indandione-1,3-bisethylene acetal with acetyl chloride in the presence of pyridine in dry THF yielded crude **8**, which upon recrystallization from ethanol-$CHCl_3$ gave a pure sample as pale yellow crystals in 70% yield; mp 210 °C. IR(KBr): 3380 (NH), 1692 (C=O), and 1610 cm^{-1}. NMR ($CDCl_3$) δ 2.16 (s, 3H, $-COCH_3$), 2.53 (s, 2H, $-O>^{-O}>CCH_2C<^{O-}_{O-}$), 4.10—4.50 (m, 8H, $-OCH_2CH_2O-$), 7.30 (t, J=7.4 Hz, 1H, aromatic H), 7.64 (d, J=7.4 Hz, 1H, aromatic H), and 8.25—8.92 ppm (m, 2H, NH plus aromatic H). Mass: *m/e* 291 (M^+), 263, 248, 247, 232, 219, 206, 205, and 191.

Found: C, 61.77; H, 5.75; N, 4.79%. Calcd for $C_{15}H_{17}NO_5$: C, 61.85; H, 5.88; N, 4.81%.

*4-Nitro-1,3-indandione-1-ethylene Thioacetal (**9**).* To a solution of 3.8 g (0.02 mol) of **1** in 140 ml of AcOH were added 1.9 g (0.02 mol) of 1,2-ethanedithiol and 2.0 g (0.01 mol) of *p*-TsOH·H_2O. The mixture was allowed to stand at room temperature overnight. Filtration of the mixture gave 60 mg (1%) of 4-nitro-1,3-indandione-1,3-bisethylene thioacetal (**10**), mp 202—205 °C, which showed no depression in the mixed melting-point test with the product obtained by the reaction of **1** with an excess 1,2-ethanedithiol. The filtrate was poured into 300 ml of water and extracted with three 50 ml portions of CH_2Cl_2. The extract was washed successively with two 300 ml portions of water, two 100 ml portions of 5% NaOH and two 200 ml portions of water. The CH_2Cl_2 solution was dried over Na_2SO_4 and then evaporated to give 2.7 g (51%) of crude monothioacetal **9**. The tlc analysis of this crude product indicated that the product consists of only **9**. Recrystallization from $CHCl_3$-hexane gave 1.9 g (36%) of **9** as pure yellow needles; mp 117—119 °C. IR (KBr): 1730 (C=O), 1530, and 1360 cm^{-1} (NO_2). NMR ($CDCl_3$): δ 3.48 (s, 2H, $-COCH_2C<^{S-}_{S-}$), 3.63 (m, 4H, $-SCH_2CH_2S-$), and 7.60—8.17 ppm (m, 3H, aromatic H).

Found: C, 49.32; H, 3.29; N, 5.03%. Calcd for $C_{11}H_9NO_3S_2$: C, 49.44; H, 3.40; N, 5.24%.

Upon acidification of the NaOH solution, 1.3 g (34%) of **1** was recovered.

*4-Nitro-1,3-indandione-1,3-bisethylene Thioacetal (**10**).* A mixture of 1.9 g (0.01 mol) of **1** and 10 ml of BF_3-etherate in 70 ml of AcOH was maintained at room temperature

overnight. The resulting solid was filtered, washed with water and then dried to give **10** as greenish yellow solid quantitatively; mp 205—207 °C. IR(KBr): 1520 and 1355 cm^{-1} (NO_2).

Found: C, 45.56; H, 3.78; N, 3.83%. Calcd for $C_{13}H_{13}NO_2S_4$: C, 45.49; H, 3.82; N, 4.08%.

4-Amino-1,3-indandione-1-ethylene Thioacetal. A suspension of 5.34 g (0.02 mol) of **9** was hydrogenated over a W-I Raney nickel in 100 ml of dioxane under atmospheric pressure at room temperature for 3 hr. The catalyst was removed by filtration. Evaporation of the filtrate left a yellow oil which was chromatographed on a neutral alumina. Elution with $CHCl_3$ gave 3.5 g (73%) of the amino compound as a pale yellow oil. IR (film): 3450, 3340 (NH_2), and 1670 cm^{-1} (C=O). The oil solidified upon distillation under reduced pressure; bp 200—210 °C/0.4 mmHg. Recrystallization from CCl_4–hexane gave an analytical sample as yellow needles; mp 94—99 °C.

Found: C, 55.56; H, 4.58; N, 5.77%. Calcd for $C_{11}H_{11}NOS_2$: C, 55.70; H, 4.64; N, 5.91%.

*4-Acetamido-1,3-indandione-1-ethylene Thioacetal (**12**).* Crude 4-amino-1,3-indandione-1-ethylene thioacetal was heated with excess Ac_2O on a water bath for 1 hr. After removal of AcOH and excess Ac_2O under reduced pressure, the residue was recrystallized from ethanol to yield **12** as light brown needles in 70% yield, mp 128—130 °C. IR (KBr): 3210—3280 (NH), 1698, and 1675 cm^{-1} (C=O). NMR ($CDCl_3$): δ 2.24 (s, 3H, $-COCH_3$), 3.49 (s, 2H, $-COCH_2-$C(S–)(S–)), 3.62 (bs, 4H, $-SCH_2CH_2S-$), 7.50 (dd, J=7.2 and 1.7 Hz, 1H, aromatic H), 7.63 (t, J=7.2 Hz, 1H, aromatic H), and 10.14—10.54 ppm (m, 1H, NH).

Found: C, 55.71; H, 4.87; N, 5.12%. Calcd for $C_{13}H_{13}NO_2S_2$: C, 55.91; H, 4.70; N, 5.02%.

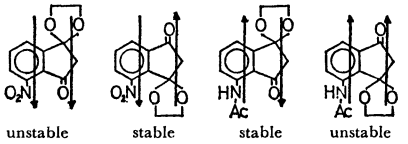
References

1) For example, C. Djerassi, "Steriod Reactions," Holden-Day, Inc., San Francisco (1963), pp. 3—5.

2) Recovery of **1** was not confirmed, since no peak due to **1** appeared in vpc ananysis of the reaction mixture.

3) Pathway through which **2** is directly transformed into **3** and *vice versa* are also possible. However, no evidence was obtained.

4) Origin of the effects of substituents on the stability of acetals is not clear. However, it seems that a dipole-dipole interaction between a substituent at the 4-position and a a carbonyl group at the 1- or 3-position is a predominant factor determining stability of the ethylene acetals.



5) It has been reported that a less hindered carbonyl group of a diketone is selectively acetalized; D. D. Chapman, W. J. Musliner, and J. W. Gates, *J. Chem. Soc., C*, **1969**, 124.

6) K. Sakaen, Y. Otsuji, and E. Imoto, unpublished results.

7) V. Oskaja and G. Vanags, *Uch. Zap. Latv. Univ.*, **57**, 67 (1964); *Chem. Abstr.*, **63**, 13129a (1965).