heterogeneous mixture was stirred and gradually warmed to room temperature (30 min). The organic layer was separated, and the aqueous phase was extracted twice with ether. The combined extracts were washed with aqueous sodium hydroxide (0.5 N), water, and brine and then dried over Na_2SO_4 and filtered. Removal of the solvent afforded a residue, which was flash chromatographed using hexane–ether (1:2) as the eluting solvent, to give the epoxide alcohol **10** (120 mg, 75% yield). Crystallization from hexane/drops of ether afforded a material with mp 121–122 °C: IR 3580–3200, 3110, 3000–2800, 1600, 1450, and 860 cm^{-1}; ^1H NMR δ 0.80 (3 H, s), 0.82 (3 H, s), 1.14 (3 H, s), 2.57 (1 H, d, J = 9.3 Hz, H-1), 3.55 (1 H, s, H-3), 4.19 (1 H, d, J = 9.3 Hz, H-2), 6.20 (1 H, m, H-β'), 7.23 (1 H, m, H-α), and 7.36 (1 H, m, H-α'). Anal. Calcd for $C_{16}H_{22}O_3$: C, 73.28; H, 8.40. Found: C, 73.28; H, 8.39.

(1*RS*,3*SR*,3a*SR*,7a*SR*)-1-(3-Furyl)-4,4a,7a-trimethyl-3,3a-epoxyhexahydroindan-2-one (11). Jones reagent (0.5 mL) was added dropwise with stirring to a solution of the epoxide-alcohol **10** (56 mg, 0.21 mmol) in acetone (6 mL) at 0 °C. The resulting mixture was stirred at 0 °C for an additional 1 h. 2-Propanol was added in small portions to discharge a brown color in the upper layer. The mixture was concentrated in vacuo to afford a residue, which was dissolved with water and extracted with ether. The organic layers were washed with water and brine, dried over Na_2SO_4, and filtered. Evaporation of the solvent left a crude which was crystallized from hexane (53 mg, 96% yield) and identified as the epoxide–cyclopentanone **11**: mp 152–154 °C; IR 3100, 3000–2800, 1750, 1460, and 890 cm^{-1}; ^1H NMR δ 0.85 (3 H, s), 0.90 (3 H, s), 1.23 (3 H, s), 3.44 (1 H, s, H-3), 3.88 (1 H, s, H-1), 6.22 (1 H, M, H-β'), 7.39 (1 H, m, H-α), and 7.44 (1 H, m, H-α'); MS m/e (relative intensity) 260 (35, M^+), 242 (13), 217 (18), 178 (21), 156 (30), 139 (32), 123 (72), 108 (90), 91 (80), 81 (100), 77 (91), 69 (64), 55 (99), and 53 (80). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.85; H, 7.69. found: C, 73.84; H, 7.68.

(1*RS*,4*SR*,4a*SR*,8a*SR*)-1-(3-Furyl)-5,5,8a-trimethyl-4,4a-epoxyoctahydro-2-benzopyran-3-one (12). A solution of *m*-chloroperbenzoic acid (52 mg, 0.30 mmol) in dry CH_2Cl_2 (1 mL) was added at room temperature to a heterogeneous solution of epoxy ketone **11** (52 mg, 0.20 mmol) in dry CH_2Cl_2 (1 mL) and $NaHCO_3$ (20 mg). The mixture was kept in the dark for 5.5 h and then diluted with ether and washed with successive solutions of $NaHSO_3$ (10%), water and brine. The organic extract was dried over Na_2SO_4, filtered, and concentrated in vacuo to afford a solid, which was flash chromatographed using hexane–ether (4:1) as the eluting solvent, to give the epoxy lactone **12** (31 mg, 60% yield). Crystallization from hexane afforded a material with mp 121–122 °C: IR 3115, 3000–2840, 1735, 1600, 1300, 1270, and 1160 cm^{-1}; ^1H NMR δ 0.81 (3 H, s), 1.09 (3 H, s), 1.21 (3 H, s), 3.64 (1 H, s, H-3), 5.58 (1 H, s, H-1), 6.33 (1 H, m, H-β'), 7.38 (1 H, m, H-α), and 7.39 (1 H, m, H-α'); MS m/e (relative intensity) 276 (19, M^+), 248 (11), 219 (40), 181 (11), 153 (100), 137 (54), 123 (100), 109 (47), 95 (52), 81 (53), 69 (40), and 55 (55). Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.56; H, 7.25. Found: C, 69.54; H, 7.25.

Registry No. **1**, 124070-88-8; **2**, 6651-36-1; (±)-**3a**, 124070-89-9; (±)-**3b**, 124151-17-3; (±)-**3c**, 124151-18-4; (±)-**4a** (isomer 1), 124070-90-2; (±)-**4a** (isomer 2), 124151-19-5; (±)-**4c** (ismer 1), 124151-20-8; (±)-**4c** (isomer 2), 124151-21-9; (±)-**5a**, 124070-91-3; (±)-**5b**, 124070-92-4; **6**, 83999-44-4; **6** ketone, 2408-37-9; (±)-**6a**, 124070-93-5; (±)-**7**, 124070-94-6; (±)-**8a**, 124070-95-7; (±)-**8b**, 124070-96-8; (±)-**9**, 124098-16-4; (±)-**9a**, 124098-15-3; (±)-**10**, 124070-97-9; (±)-**10a**, 124070-98-0; (±)-**11**, 124070-99-1; (±)-**12**, 124071-00-7; 3-Fur-CHO, 498-60-2; *n*-$C_3H_7NO_2$, 108-03-2; ethyl 2-oxocyclohexanecarboxylate, 1655-07-8.

Notes

Reduction of α-Diketones and α-Keto Esters with HI in Acetic Anhydride–Acetic Acid

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Introduction

The reduction of α-keto-substituted carbonyl compounds by aqueous HI–acetic acid solutions has been known for a long time.[1-4] With the notable exception of the reduction of benzil derivatives, which cleanly generate benzoins upon reduction, the reaction has been reported to result in the net deoxygenation of the reduced carbonyl according to eq 1. α-Hydroxy ketones are rarely observed as minor byproducts, and the reaction has seen limited application.

$$RC(=O)C(=O)R' + 4HI \rightarrow RCH_2C(=O)R' + 2I_2 \quad (1)$$

We recently had cause to reexamine this rather interesting reduction of α-keto-substituted ketones and esters with HI. However, unlike the previous examinations, we were operating our system under anhydrous conditions using a solution of acetic anhydride–acetic acid in place of aqueous acetic acid. We found that the reaction provided an efficient reduction of the α-keto-substituted carbonyl compound to α-acetoxy ketones without any significant deoxygenation as reported in the earlier reports. The α-acetoxy ketones and esters obtained by this process are useful as flavoring and fragrance components of a variety of foods and beverages,[5] and we would like to discuss the details of this investigation in the remainder of this report.

Results

We would like to begin this discussion by focusing on the simplest α-diketone, 2,3-butanedione (commonly referred to as biacetyl). When we added biacetyl to a solution of HI in acetic anhydride–acetic acid at room temperature, we received a rapid, exothermic reduction of the biacetyl to acetoin acetate in quantitative yield with the

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(2) (a) Reusch, W.; LeMahieu, R. *J. Am. Chem. Soc.* **1964**, *86*, 3068, and references therein. (b) Reusch, W.; LeMahieu, R. *J. Am. Chem. Soc.* **1963**, *85*, 1669.
(3) (a) Nakai, T.; Mimura, T. *J. Synth. Chem. Jpn.* **1977**, *35*, 964. (b) Talapatra, S. K.; Pradhan, D. K.; Takapatra, B. *Ind. J. Chem., Sect. B* **1978**,16, 361. (c) Duddeck, H.; Wiskamp, V.; Rosenbaum, D. *J. Org. Chem.* **1981**, *46*, 5332. (d) Osman, S. M.; Ahmad, M. *Fette, Seifen, Anstrichm.* **1970**, *72*, 454 (Chem. Abstr. 73:44844q). (e) Rakhit, S.; Gut, M. *J. Org. Chem.* **1968**, *33*, 1196.
(4) Reports of the corresponding reduction of α-keto esters and acids have been limited to the reduction of pyruvic acid to propionic acid in concentrated aqueous HI solutions. See: (a) Kaplan, L. *J. Org. Chem.* **1982**, *47*, 5422. (b) Wislicenus, W. *Justus Liebigs Ann. Chem.* **1863**, *126*, 229.
(5) See, for the example: (a) Oser, B. L.; Ford, R. A. *Food Technol. (Chicago)* **1978**, *32*(2), 60. See also: (b) Schreier, P. *J. Agric. Food Chem.* **1980**, *28*, 926, and references therein.

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Table I. Reductive Acetylation of α-Carbonyl-Substituted Ketones with HI–Ac_2O

$RC(=O)C(=O)R' + HI + Ac_2O \rightarrow RCH(OAc)C(=O)R' + I_2 + AcOH$

	starting mater		product				
ex	R	R′	R	R′	yield,[a] %	temp, °C	ref
1	Me	Me	Me	Me	100[b]	RT	6
2	Ph	Ph	Ph	Ph	99	RT	7
3	Et	Et	Et	Et	88	RT	c
4[d]	Ph	Me	Ph	Me	55	RT	8a–c
			Me	Ph	37		8b–d
5	Ph	OMe	Ph	OMe	95	70–75	9
6	Me	OEt	Me	OEt	78	70–75	10
7[d]	*i*-Pr	OEt	*i*-Pr	OEt	77	70–75	5b
			$(CH_3)_2C{=}C(OAc)CO_2Et$		20		11
8	$-C(CH_3)_2CH_2O-$		$-C(CH_3)_2CH_2O-$		50	50–55	12
9	$-CO_2Et$	OEt	$-CO_2Et$	OEt	88	50–55	13
10[e]	Et	Et	$EtCO_2CH(Et)C(=O)Et$		98	RT	c

[a] All yields are for isolated materials except where noted. [b] Determined by GC. The reported yield is for the range of yields obtained over multiple runs. [c] These are new compounds. Full characterization appears in the Experimental Section. [d] Product distributions determined by integration of the ^1H NMR spectrum of the mixture isolated as described in the Experimental Section. [e] Propionic anhydride was substituted for acetic anhydride on a molar basis.

cogeneration of molecular iodine.

The earlier descriptions of HI reductions in these systems proposed α-hydroxy ketones as intermediates in the deoxygenation of the α-keto carbonyl compounds. Under our conditions, we believed our reaction was analogous but that, by running the reaction in the presence of acetic anhydride, we were capturing the α-hydroxy ketone intermediate by esterification.

So that we could correlate our observations with the earlier reports, we briefly examined the biacetyl system and its reduction in aqueous acetic acid to verify the existence of the aforementioned α-hydroxy ketone intermediate. When biacetyl is added to an aqueous HI–acetic acid system containing 2 mol equiv of HI and the products examined by GC, the reaction is not complete, giving a mixture of biacetyl and acetoin. We suspected that the initial reaction of HI with biacetyl was an equilibrium, which we have denoted by eq 2. We sought to prove this

$$CH_3C(=O)C(=O)CH_3 + HI \rightleftharpoons CH_3CH(OH)C(=O)CH_3 + I_2 \quad (2)$$

by demonstrating the back reaction. Addition of acetoin to an aqueous iodine–acetic acid system resulted in the generation of measurable quantities of biacetyl, clearly demonstrating that the reaction is reversible. We attempted to establish an equilibrium constant for the reaction but failed as the solutions were unstable, giving products from additional reactions, particularly acetoin acetate. This rendered the data useless for this quantitative measurement.

The earlier reports contrast with our reaction in that we operate at a lower temperature and, as mentioned earlier, we are operating under anhydrous conditions in the presence of acetic anhydride. In the earlier reports, it would appear that the reaction is driven to completion by the subsequent reduction of the α-hydroxy ketone, whereas in our system the reaction is driven to completion by the exothermic acylation of the hydroxy intermediate.

We examined a number of α-keto-substituted ketones and esters using an experimental protocol in which a solution of aqueous HI (3 mol equiv) was added to excess acetic anhydride to reduce a mole of ketone. The results are summarized in Table I.

Focusing on the reduction of α-diketones (examples 1–4,10), we found the reaction to be a very high-yield reaction but not very regioselective even when the ketones were obviously different such as in example 4 (Table I). The lack of selectivity limits this reaction's practical utility in organic synthesis for the reduction of α-diketones. One important observation is that with the α-diketones, we never detected any further reduction, enol ester formation (from product or starting material), or any iodination.

Although the earlier literature made sparse reference to the reduction of α-keto esters or acids, we were able to demonstrate that the HI–acetic anhydride mixture could also be used to efficiently reduce these compounds, although higher temperatures are required to reach acceptable rates and the yields are slightly lower. We presume that the need for higher temperatures is a result of equilibrium 2, which would be presumed to be much less favorable than in the case of α-diketones.

We have shown several examples in Table I but would like to focus on one important result, shown in example 7. In the reduction of ethyl 3-methyl-2-oxobutanoate (example 7), we were able to establish that the product, based on NMR integration, was an 80:20 mixture of the reduced product (ethyl 3-methyl-2-acetoxybutanoate) and the enol acetate (ethyl 3-methyl-2-acetoxy2-buten-1-oate). This clearly indicates that, with the slower reduction of α-keto esters, the acetylation of the enol form can compete, particularly if the starting material is sterically congested.

As demonstrated by example 10, the reaction is not restricted to acetic anhydride. We have substituted pro-

(6) This material has innumerable references in the literature and is an important flavoring agent in a number of foods and beverages. See ref 5 for examples.

(7) A number of references to this compound exist. For an example, see: Corson, B. B; Saliani, N. A. *Org. Synth. Coll. Vol. II* **1943**, 69.

(8) (a) Gisselbrecht, J.; Henning, L. *Acta Chem. Scand. B* **1985**, *39*, 823. (b) Kelder, J.; Cerfontain, H.; Van der Weilen, F. W. M. *J. Chem. Soc., Perkin Trans. 2* **1977**, 710. (c) Rubin, M. B.; Inbar, S. *Tetrahedron Lett.* **1979**, 5021. (d) Shono, T.; Nishiguchi, I.; Nitta, M. *Chem. Lett.* **1976**, 1319.

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(10) This compound has a large number of references in the literature. For examples, see ref 5b and the following: (a) Cohen, S. G.; Crossley, J.; Khedouri, E.; Zand, R.; Klee, L. H. *J. Am. Chem. Soc.* **1963**, *85*, 1685. (b) Rahm, A.; Pereyre, M. *Bull Soc. Chim. Belg.* **1980**, *89*, 843.

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(12) (a) Inagaki, M.; Kuniyoshi, I.; Saburo, N. *Yakugaku Zasshi* **1976**, *96*, 71. (b) Oi, N.; Takai, R.; Kitihara, H. *J. Chromatogr.* **1983**, *256*, 154. (c) Yamamoto, J.; Katoaka, K.; Akazawa, O. *Yakugaku Zasshi* **1977**, *97*, 151.

(13) There are a number of references to this compound. For examples, see ref 12a and the following (a) Mandel'shtam, T. V.; Kharicheva, E. M.; Kurchasova, N. A. *Zh. Org. Khim.* **1976**, *12*, 2626. (b) Pellicciari, R.; Curini, M.; Ceccherelli, P.; Natalini, B. *Gazz. Chim. Ital.* **1978**, *108*, 671.

pionic anhydride for acetic anhydride in the reduction of 3,4-hexanedione and found that the reaction is equally facile, yielding 4-oxo-3-hexyl propanoate in 98% yield.

Summary

We have examined the reduction of α-diketones and α-keto esters in HI–acetic anhydride mixtures and found that the reaction gives good-to-excellent yields of α-acetoxy ketones and esters.

Experimental Section

All the starting α-diketones and α-keto esters were available from Aldrich Chemical Co., Milwaukee WI. Acetylated biacetyl (3-acetoxy-3-buten-2-one) used for GC comparison was obtained by the method of Ardecky et al.[14]

General Procedure for the Reduction of α-Diketones and α-Keto Esters. A 30-mL sample of acetic anhydride was chilled on ice, and then 8.2 g of 47% aqueous HI (30 mmol of HI) was added slowly to the magnetically stirred solution. **Caution**: The reaction of aqueous HI and acetic anhydride is very exothermic and can be deceptive as there is a variable induction period of several seconds to a couple of minutes. Therefore it is imperative that the addition be performed cautiously. After addition was complete, the reaction was allowed to stir an additional 5–10 min. During the course of the reaction the stabilizer (H_3PO_2, an oxidation inhibitor) usually added to HI precipitates, and the solid impurity is removed by filtration through a fine fritted-glass filter. The resultant solution, which can be colored anywhere from grey to orange–red depending on the source of the HI, is added to a 100-mL round-bottomed flask, and 10 mmol of the α-keto carbonyl compound added. In the case of α-diketones the reduction was performed at room temperature with stirring at room temperature for 15–20 min, while α-keto esters were reduced at elevated temperatures (at either 50–55 or 70–75 °C as indicated in Table I) for 30 min.

The product was isolated[15] by adding 10% aqueous sodium bisulfite, cautiously at first, to the reaction mixture until the orange color of iodine is completely dissipated.[16] The reaction mixture was then added to a 250-mL separatory funnel, and 100 mL of distilled water added. The aqueous layer was extracted three times with diethyl ether. The ether layers were combined and back extracted twice with 50-mL washes of distilled water, with a wash of 50 mL of 10% NaOH, and finally with an additional 50 mL of distilled water. The ether layer was dried over K_2CO_3 (except in example 9, where Na_2SO_4 was used instead) and then filtered. The ether was then removed in vacuo. In most cases no further refinement was necessary, but further purification could be accomplished by simple distillation in a Kugelrohr oven when desired with little loss in yield. With the exception of 4-acetoxy-3-hexanone and 4-oxo-3-hexyl propanoate (examples 3 and 10, respectively) all the products were known in the literature and were identified on the basis of their spectroscopic properties. The appropriate literature references appear in Table I. These literature references are not exhaustive as some of these compounds have many citations.

4-Acetoxy-3-hexanone. Following the general procedure, 3,4-hexanedione was converted to 4-acetoxy-3-hexanone in 88% yield: 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.98 (t, 3 H), 1.08 (t, 3 H), 1.68–1.92 (m, 2 H), 2.17 (s, 3 H), 2.35–2.62 (m, 2 H), 4.98 (dd, 1 H, J = 5, 8 Hz); 75-MHz ^{13}C NMR ($CDCl_3$) 7.3, 9.7, 20.8, 24.1, 32.2, 79.8, 171.4, 208.9; IR (CH_2Cl_2) 1730 m^{-1} (vs, br); MS (50 eV) m/e = 43, 57, 101, 115, 129, 158; exact mass calcd for $C_8H_{14}O_3$ 158.0943, found 158.0952.

4-Oxo-3-hexyl Propanoate. Following the general procedure, 3,4-hexanedione was converted to 4-oxo-3-hexyl propanoate in 98% yield: 300-MHz ^{1}H NMR ($CDCl_3$) δ 0.98 (t, 3 H), 1.08 (t, 3 H), 1.20 (t, 3 H), 1.68–1.92 (m, 2 H), 2.30–2.65 (m, 4 H), 4.98 (dd, 1 H, J = 5, 8 Hz); 75-MHz ^{13}C NMR ($CDCl_3$) δ 7.3, 9.1, 9.7, 24.2, 27.5, 32.2, 79.6, 174.9, 209.1; IR (CH_2Cl_2) 1730 cm^{-1} (vs, br); Ms (50 eV) m/e = 57, 114, 115, 143, 172; exact mass calcd for $C_9H_{16}O_3$ 172.1100, found 172.1109.

Acetyl Acetoin. Acetyl acetoin used in GC analyses could be generated by the literature reference,[10a] but a more convenient method was to add an 85% aqueous solution of acetoin (3-hydroxy-2-butanone, obtained from Aldrich Chemical Co.) in several small portions to a mixture of 60 mL of acetic anhydride and 0.9 g of Amberlyst-15. The reaction predictably undergoes an exothermic reaction. Gradually, over the 1.5-h reaction period, the reaction turns orange–brown. The solution is filtered to remove the Amberlyst-15 resin and distilled at 12 mmHg to give 24.25 g of acetyl acetoin boiling between 62–65 °C (yield based on 85% acetoin: 69%).

Acknowledgment. We would like to thank Onzie Woods for his assistance in performing the GC analyses for biacetyl and its reduction products.

Registry No. MeC(=O)C(=O)Me, 431-03-8; PhC(=O)C(=O)Ph, 134-81-6; EtC(=O)C(=O)Et, 4437-51-8; PhC(=O)C(=O)Me, 579-07-7; PhC(=O)C(=O)OMe, 15206-55-0; MeC(=O)C(=O)OEt, 617-35-6; i-PrC(=O)C(=O)OEt, 20201-24-5; $C(CH_3)_2CH_2OC(=O)C(=O)$, 13031-04-4; $EtCO_2C(=O)C(=O)CO_2Et$, 59743-08-7; MeCH(OAc)C(=O)Me, 4906-24-5; PhCH(OAc)C(=O)Ph, 574-06-1; EtCH(OAc)C(=O)Et, 99768-38-4; PhCH(OAc)C(=O)Me, 19275-80-0; MeCH(OAc)C(=O)Ph, 19347-08-1; PhCH(OAc)C(=O)OMe, 947-94-4; MeCH(OAc)C(=O)OEt, 2985-28-6; i-PrCH(OAc)C(=O)OEt, 74108-96-6; $(CH_3)_2C{=}C(OAc)CO_2Et$, 85801-14-5; $C(CH_3)_2CH_2OCH(OAc)C(=O)$, 123241-21-4; $EtCO_2CH(OAc)C(=O)CO_2Et$, 99173-90-7; $EtCO_2CH(Et)C(=O)Et$, 117090-85-4; HI, 10034-85-2; $CH_2C(=O)CH(OH)CH_3$, 513-86-0.

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(15) All the yields listed in Table I are for compounds that were isolated by the described procedure with the exception of the reduction of biacetyl described in example 1, which could not be readily isolated by this procedure and was determined by GC and verified by comparison of its GC–MS with genuine material.

(16) We verified that the reduction was not caused by bisulfite by examining a biacetyl reduction with and without the addition of bisulfite at the end of the reaction. There was no discernible difference between the two reactions.

Structure and Reactivity in 9,10-Bridged Anthracenes

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Interest in [n]paracyclophanes (1) has continued unabated.[1] Synthetic success has been hard won, beginning with Allinger's prediction of the feasibility of [7]paracyclophane synthesis[2] and his much later accomplishment of that goal.[3] Since then, [6]paracyclophane targets[4] have fallen and [5]paracyclophane, initially invoked as a transient intermediate in the pyrolysis of the corresponding Dewar isomer, has been prepared and observed at low temperature.[5] Recently, [4]paracyclophane has been

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