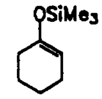
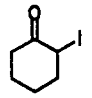
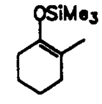
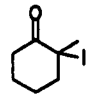
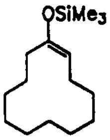
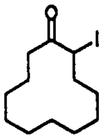
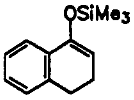
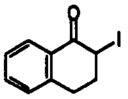
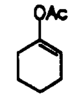
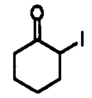
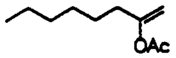
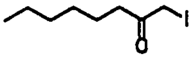
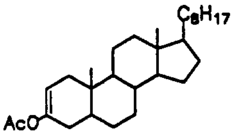
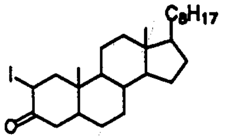
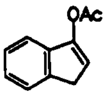
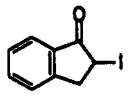
Table I. Preparation of α-Iodo Ketones from Enol Silyl Ethers and Enol Acetates with Copper(II) Nitrate and Iodine

substrate	product	yield[a] (%)
 1a	 2a	100
 1b	 2b	100
 1c	 2c	85
 1d	 2d	85
 1e	 2a	100
 1f	 2f	90
 1g	 2g	100
 1h	 2h	100

[a] Isolated yield.

convenient procedure for the regiospecific synthesis of α-iodo ketones. This method supplements the others already reported and recommends itself for the simplicity, the mild conditions needed, and the high yields obtained.

Experimental Section

Enol acetates and enol silyl ethers were prepared according standard procedures.[11,12] All known compounds were identified by comparison of their IR, ^{1}H NMR, and MS spectra with the published data,[14] except for compound **1h**, which has been synthesized for the first time.

1*H*-Inden-3-yl acetate (1h) was prepared according to the method of ref 11 and purified by column chromatography on silica gel (hexane/ethyl acetate (10:1)): mp 46–47 °C; IR (neat) 1775, 1710 cm^{-1}; ^{1}H NMR (80 MHz, CDCl$_3$) δ 7.5–7.1 (m, 4 H), 6.32 (t, J = 2 Hz, 1 H), 3.40 (d, J = 2 Hz, 2 H), 2.32 (s, 3 H); MS m/z 174. Anal. Calcd for $C_{11}H_{10}O_2$: C, 74.84; H, 5.78. Found: C, 74.92; H, 5.55.

Preparation of α-Iodo Ketones 2. 2-Iodocyclododecanone (2c). To a solution of I_2 (0.157 g, 1.25 mmol) and $Cu(NO_3)_2\cdot H_2O$ (0.301 g, 1.25 mmol) in 5 mL of CH_3CN was added (trimethylsiloxy)cyclododecene (0.317 g, 1.25 mmol).[18] After 5 min, the reaction mixture was diluted with pentane (10 mL), washed with saturated sodium thiosulfate solution (10 mL), and then dried (Na_2SO_4). After concentration the residue was crystallized from methanol to give 0.326 g (85%) of pure 2-iodocyclododecanone, mp 53–54 °C (lit.[7] mp 52–52.5 °C).

Reaction times for enol silanes and enol acetates were 5 and 15 min, respectively. In those cases in which yields of 100% are reported, it means that no further purification was done. The purity of the products was checked by ^{1}H NMR and GC. No trace of starting material or other products different from the corresponding iodo ketone were detected. Products **2g**, **2d**, and **2h** have been crystallized; compound **2f** has been purified by flash chromatography on silica gel (hexane/ethyl acetate (8:2)).

2α-Iodo-5α-cholestan-3-one (2g): mp 131.5–132.5 °C (lit.[16] mp 132–133 °C).

2-Iodo-1-tetralone (2d): mp 77–78 °C (lit.[2] mp 76–78 °C).

2-Iodo-1-indanone (2h): mp 69–70 °C (lit.[17] mp 68–70 °C).

Acknowledgment. This work has been carried out in the framework of the Progetto Finalizzato CNR Chimica Fine II.

Registry No. **1a**, 6651-36-1; **1b**, 19980-35-9; **1c**, 51584-36-2; **1d**, 38858-72-9; **1e**, 1424-22-2; **1f**, 26735-84-2; **1g**, 1255-89-6; **1h**, 19455-83-5; **2a**, 35365-19-6; **2b**, 77256-25-8; **2c**, 69381-33-5; **2d**, 41099-31-4; **2f**, 63641-50-9; **2g**, 2516-55-4; **2h**, 113021-30-0; Cu(NO_2)$_2$, 3251-23-8; I_2, 7553-56-2; PhOMe, 100-66-3; iodoanisole, 35745-35-8.

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(11) Torii, S.; Inokuchi, T.; Misima, S.; Kobayashi, T. *J. Org. Chem.* **1980**, *45*, 2731.

(12) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

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(14) For compounds **1a**, **2a**, **1c**, **2c**, see ref 7; **1b**, **2b**, ref 15; **1d**, **2d**, **1e**, **1f**, **2f**, ref 2; **1g**, **2g**, refs 4, 16; **2h**, ref 17.

(15) Rubottom, G. M.; Mott, R. C.; Juve, H. D., Jr. *J. Org. Chem.* **1981**, *46*, 2717.

(16) Horiuci, C. A.; Satoh, J. Y. *Synthesis* **1981**, 312.

(17) Sket, B.; Zupan, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 4489.

(18) For the acetate **1g** 2 mL of CH_2Cl_2 was added to achieve the complete solubilization of the substrate.

Benzoin Enediol Dianion and Hydroxide Ion in DMSO: A Single Electron Transfer Reduction System Driven by the Irreversible Benzilic Acid Rearrangement

J. Michael Robinson,* Emmette T. Flynn,
Terry L. McMahan, and Sharai L. Simpson

Department of Chemistry, The University of Texas of the Permian Basin, Odessa, Texas 79762

John C. Trisler and Kenneth Bruce Conn

Department of Chemistry, Louisiana Tech University, Ruston, Louisiana, 71270

Received March 26, 1991

In a study of nucleophilic reactions of ketone enolate ions with the sterically constrained (Z)-α,β-dibenzoylstyrene (1) in DMSO, a reductive side reaction was found.[1] The competing reduction was proposed to occur by elec-

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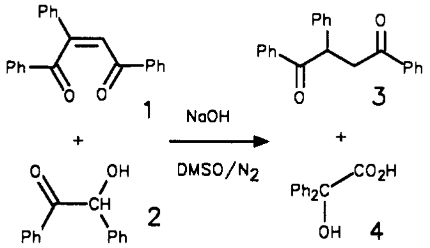
(1) Taken in part from: Robinson, J. M. M.S. Thesis, Louisiana Tech University, 1969.

tron transfer from an enolate ion. This proposal led to the use of benzoin enediol dianion (**6**) as a new irreversible electron-transfer reducing agent. We now report this and related reductions that lend support to the proposed single electron transfer (SET) mechanism.

1 reacted with benzoin (**2**) in DMSO containing an excess of sodium hydroxide for 2 h under an inert atmosphere. The reaction (green color) afforded essentially quantitative yields of 1,2,4-triphenyl-1,4-butanedione (**3**)[2] and benzilic acid (**4**). A similar reaction conducted with sodium hydride as base gave only an 80% conversion of **1** to **3**. With no hydroxide ion present, benzil (**8**) and benzoin benzoate were found as well as benzoic acid and benzilic acid. Such products might be expected to form, without a proton source, according to known cleavage reactions of benzil in DMSO.[3] The orange-red color of the latter reaction indicated a greater concentration of the benzoin dianion (**6**),[4a,b] while the green color of reactions with only sodium hydroxide as base indicated a mixture of **6** and the blue anion radical **7**.[4c–e] When **1** and **2** are reacted with sodium hydroxide and excess sodium hydride, the reaction (orange) affords only **3** and **4**. Water produced as a byproduct of using only sodium hydroxide as base apparently has no important role in the reaction. In this case the presence of hydroxide ion, generated in situ from water and excess sodium hydride, precludes the more complex cleavage reactions of benzil.

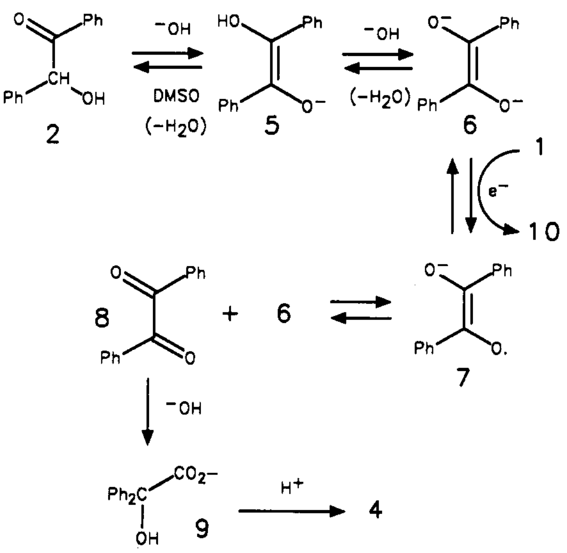


Benzoin (**2**) was chosen as an ideal reactant becuase its tendency in basic solution to form the colorful benzil anion radical (**7**) by electron transfer from the enediol dianion **6** is well-known.[4] Furthermore, **7** is known to undergo a reversible disproportionation to benzil (**8**) and **6**. When this occurs under our reaction conditions, **8** reacts with the excess hydroxide ion giving the benzilic acid rearrangement (BAR).[5] Such an irreversible rearrangement drives all the equilibria to the right. Scheme I shows the proposed driven reduction mechanism. Benzil (**8**) was isolated from a reaction conducted for a short time. Traces of **8** are always returned from the BAR. Benzilic acid (**4**) apparently forms more slowly than **3** under these conditions. Oxygen interferes with these reductions so they must be conducted in an inert atmosphere. The reduction potential of oxygen (E_{red} = −0.73 V in base)[6a,7] is much more favorable for an electron-transfer reaction than most organic substrates.[4a,d,6]

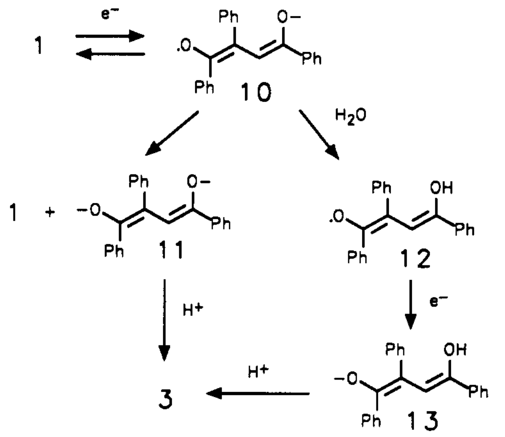
Reduction of Substrates

When **6** transfers a single electron to enone **1** (Scheme II), the anion radical **10** results. Cyclic voltammetry indicates that **10** is very short lived.[8] Thus, **1** readily undergoes an electron transfer followed by a chemical reaction, or an EC process in electrochemical terms.[9] Since **1** is reduced to the dihydro **3** even in the absence of proton donors (i.e., in reactions with excess sodium hydride), this suggests that the chemical reaction of **10** is a rapid disproportionation to **1** and the sterically favorable resonance-stabilized dianion **11**. Disproportionation of the semidione **10** can be easily rationalized if it is considered to be a vinylogue of the benzoin anion radical (**7**) for which such disproportionation is well-known. It is also possible that anion radical **10** could be neutralized to a simple radical **12** by the proton sources available when only sodium hydroxide is used, i.e., water, benzoin (**2**), and benzoin monoanion (**5**). This radical could receive another electron from **6** (or **7**) to give a monoanion **13**, which is eventually protonated to form **3**. Such an electron transfer followed by a chemical reaction and then by another electron transfer represents the ECE process common in

Scheme I



Scheme II



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(3) (a) Trisler, J. C.; Freasier, B. F.; Wu, S.-M. *Tetrahedron Lett.* **1974**, 687. (b) Hsieh, S. Y. M.S. Thesis, Louisiana Tech University, 1975.

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(6) (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 701. (b) Russell, G. A.; Moye, A. J.; Nagpal, K. *J. Am. Chem. Soc.* **1964**, *84*, 4154. (c) Philip, R. H., Jr.; Flurry, R. L.; Day, R. A., Jr. *J. Electrochem. Soc.* **1964**, *111*, 328.

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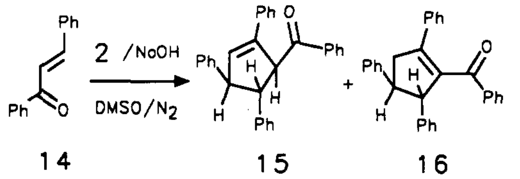
(8) Winecoff, W. F., III; O'Brian, F. L.; Boykin, D. W., Jr. *J. Org. Chem.* **1973**, *38*, 1474.

(9) Fry, A. J. *Synthetic Organic Electrochemistry*, 2nd ed.; Wiley: New York, 1989.

organic electrochemistry.[9] Either of these reduction paths (EC or ECE) is favored over the anion radical receiving a second electron to form a dianion. Not only is the second reduction potential of an enone to a dianion more difficult[4a,10] but there is no electrochemical evidence for an electron transfer to anion radical **10**.[8]

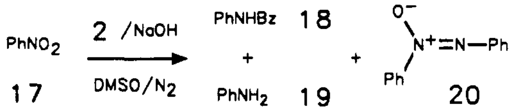
In support of a single electron transfer (SET) mechanism, chalcone (**14**) was reduced to dihydro dimers that were subsequently cyclized by this reagent system.[11] Thus, **14** was reacted with benzoin (**2**) and NaOH for 4 h (green) to afford 5-benzoyl-1,3,4-triphenylcyclopent-1-ene (**15**) (~72%, see Experimental Section) and 2-benzoyl-1,3,4-triphenylcyclopent-1-ene (**16**) (~28%). The ratio of **15** to **16** was reversed (29:71) when the reaction was conducted with sodium hydroxide and excess sodium hydride for a longer time (red).



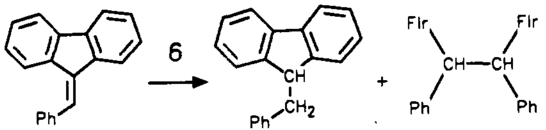
14 15 16

The structures and stereochemistry of **15** and **16** and their dideuterio analogues[11] have been proven by syntheses as well as by spectral data.[12] They have been produced from chalcone (**14**) by many types of electron-transfer reduction agents such as VCl$_2$,[12a] sodium,[12d] anthracene anion radical,[13] and electrochemical means.[14] Studies have shown that when the chalcone anion radical forms it couples to 1,3,4,6-tetraphenylhexane-1,6-dione dianion, which then cyclizes to the alcohol and dehydrates to **15**. **15** is converted to **16** by base.[12b] When the reaction was conducted with 2:1 mole ratio of **14** and **2**, we anticipated the absence of unreacted benzoin (**2**) would have facilitated isolation of products. However, some higher molecular weight products were also formed that we believe to be the known trimers of **14**. More importantly, GC/MS analyses of all reactions of **14** showed no trace of 1,3-diphenyl-1-propanone, which would be the major product expected if hydride or a two-electron transfer were occuring.[13] Therefore, we conclude that a similar SET reduction takes place with chalcone (**14**) and benzoin enediol dianion (**6**) as depicted in Scheme I.

Benzoin (**2**) has until now seldom been used to reduce other substrates.[15] Nitrobenzenes were reduced with 1 molar equiv of **2** in alcoholic base to azoxybenzenes.[16] So, we also reduced nitrobenzene (**17**) but with enough **6** theoretically to produce aniline. Most of the incipient aniline (**20**) was trapped by a benzil cleavage reaction as benzanilide (**18**). The N–N coupled compound, azoxybenzene (**19**), only accounted for about 34% of the yield. No further attempt was made to study the nitrobenzene substrate.



Our reductions of nitrobenzene (**17**) and unsaturated ketones **1** and **14** only represented two types of substrates with E_{red} of −1.01,[6a] −1.19,[7,17] and −1.41 V,[18] respectively, in DMF. Therefore, we chose to react a hydrocarbon substrate, 9-benzalfluorene (**21**) with even a more difficult reduction potential (E_{red} = −1.5 V in DMF/H$_2$O).[19] This reaction was slower as expected and in accord with the E_{red}. By use of the NaOH only conditions (green), less than 10% of the starting material had reacted in 6.5 h. 9-Benzylfluorene (**22**) was the major product. However, a similar reaction with conditions of excess NaH (dark red) was almost completely reduced in the same amount of time. Reduction occurred to give predominantly (82%) the hydrodimer 1,2-diphenyl-1,2-bis(9-fluorenyl)ethane (**23**) and to a much lesser extent (6%) 9-benzylfluorene (**22**). **23** was the major product of reported electrolysis experiments.[19]



21 22 23

The E_{red} limit for compounds reduced by this system is particularly interesting in view of such an irreversible step, the benzilic acid rearrangement, to assist perhaps poorly favorable equilibria. According to House and Weeks,[18] the propensity of an initial transfer of an electron from an anion to a simple enone can be estimated from a comparison of the electrode potential E_{red} of the enone and the electrode potential E_{ox} of the anion. They found that when $E_{red} - E_{ox}$ was greater than −0.4 V the concentration of anion radical became significant (10^{-4} M or greater). Thus, we can estimate the *effective* E_{ox} of this reduction system to be −1.1 V and perhaps even more negative. The polarographic $E_{1/2}$'s of benzil (**8**) in DMSO are −1.01 and −1.76 V[20] and represent the anion radical **7** and the enediol dianion **6**. Thus, the maximum E_{ox} of **6** could be −1.76 V in DMSO. However, the presence of water may shift the second potential to somewhat higher (more positive) value.[4a,10] Consequently, the greater concentration of **6** and the absence of water obtained in reactions utilizing excess sodium hydride (orange-red) will maintain the strongest reaction potential. Such a change in potential and in the driving force(s) for reaction was clearly demonstrated in the reactions with **21**.

Conclusion

A range of substrates have been reduced by benzoin and hydroxide ion in DMSO. Benzoin is oxidized during the process to benzil, which is then converted irreversibly to benzilic acid. This driven redox reaction may represent the first practical use of the benzilic acid rearrangement.

The dimeric reduction products obtained with three of these substrates are the same products that are shown in the literature to be produced by known SET reactions. Formation of such products is difficult to explain by any means other than by radical coupling. Furthermore, ox-

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(15) Recently, the surface of Teflon has been reduced by **6** to a reactive, halogen-free surface. (a) Costello, C. A.; McCarty, T. J. *Macromolecules* **1984**, *17*, 2940. (b) Iqbal, Z.; Ivory, D. M.; Szobota, J. S.; Elsenbaumer, R. L.; Baughman, R. H. *Ibid.* **1986**, *19*, 2992.

(16) Nisbet, H. B. *J. Chem. Soc.* **1927**, 2081.

(17) According to the mechanism presented (EC), only the first reduction potential needs to be achieved.

(18) House, H. O.; Weeks, P. D. *J. Am. Chem. Soc.* **1975**, *97*, 2778 and accompanying papers.

(19) Baizer, M. M.; Anderson, J. D. *J. Org. Chem.* **1965**, *30*, 1348.

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ygen quenching, electrochemical evidence, and our rough correlation of potentials with reactivity of substrates lend strong support to our proposed SET mechanism.

We are continuing to evaluate reagents of this type to determine the scope of functional groups reduced and their E_{red} limit as well as the E_{ox} limit of other aryl enediol dianions.

Experimental Section

General. Benzoin (2) and chalcone (14) (Aldrich) were recrystallized from EtOH before use. DMSO was distilled from CaH_2 at reduced pressure (~20 mm) and stored under N_2, NaOH was ground to a fine powder just before use. NaH was weighed as a 56% suspension in mineral oil. It was necessary to wash the oil from the NaH powder in the reaction flask or reactions usually did not proceed. The wash was performed with petroleum ether under N_2. After standing for a short time, the solvent wash could be easily decanted. Reactions were stopped, and the DMSO was removed by pouring the solution into several hundred mL of acidified water (HCl) and extracting into Et_2O, which was then washed with water. The DMSO-free ether extracts were further divided into Al and N fractions by standard bicarbonate extraction procedures. Final ether extracts were dried with $CaCl_2$ or anhydrous Na_2SO_4. Fractions were usually analyzed by GC/MS (EI and CI-H_2 modes) or by HPLC/PB/MS before recrystallization and/or preparative chromatography. GC employed a HP-1 (0.2 mm i.d. × 12.5 m and 0.33 μm film, $\beta = 150$) capillary column. HPLC used a 5-μm Resolve C18 column with $MeOH/H_2O$ solvents. Preparative plate chromatography was done on 20 × 20 cm silica gel 60 (PLK-F254) plates. Suitable spectra (IR, NMR, MS) were obtained to match literature data for all known compounds. Melting points were taken in capillary tubes and are reported uncorrected in degrees C. A few representative procedures are included.

(*Z*)-α,β-Dibenzoylstyrene (1), Benzoin (2), and NaOH. 1 (1.56 g, 5.0 mmol) and 2 (1.06 g, 5.0 mmol) were dissolved in 25 mL of DMSO. NaOH (0.61 g, 15.0 mmol) was added and the mixture stirred at rt for 2 h. The neutral layer gave on evaporation nearly pure 1,2,4-triphenyl-1,4-butanedione (3, 1.59 g, ~100%) of mp 119–125.5 °C. The mp was suppressed by the presence of a small amount of yellow benzil (8). One recrystallization from EtOH gave 1.45 g (91%) of colorless 3: mp 124.5–126 °C (lit.[2] mp 126 °C). The Al fraction eventually gave 1.05 g (91.4%) of crude benzilic acid (4), mp 139.5–146 °C (and mp 146.5–148.5 °C from hexane/acetone). In a duplicate reaction, which was allowed to proceed only 15 min, a small quantity of each, benzil (8) and benzoin (2), were isolated.

Chalcone (14), 2, and NaOH. 14 (4.16 g, 20.0 mmol) and 2 (2.12 g, 10.0 mmol) were dissolved in DMSO (50 mL) containing NaOH (11.2 mmol) prepared in situ by NaH/oil (0.48 g) and distilled water (0.32 g, 17.8 mmol). After being stirred for 4 h under N_2 atmosphere, the dark green solution was worked up as usual. Evaporation of the neutral layer and drying in a vacuum desiccator afforded a very viscous oil (4.12 g), part of which (1.57 g) was placed on a column of alumina (60 mL Alcoa F-20) and developed with petroleum ether. Elution with 2% Et_2O in petroleum ether afforded 5-benzoyl-1,3,4-triphenylcyclopent-1-ene (15) (0.31 g, 20.3%), mp 177–179 °C (lit.[12d] mp 181–182 °C). Continued elution afforded 2-benzoyl-1,3,4-triphenylcyclopent-1-ene (16, 0.34 g, 22.3%), mp 121–122 °C (lit.[12a] mp 123 °C).

The Al fraction gave a crude acid product (1.24 g, 54.4%) that was recrystallized from acetone/hexane to give 4: mp 138–140 °C.

A similar reaction of 14 and 2 with powdered NaOH was conducted with a 1:1:3 mole ratio for 4 h (green). Analysis by GC/MS gave 15 (71.6%, mixture of 3 isomers) and 16 (27.7%, mixture of 2 isomers). About 0.7% of 14 remained. As expected, 1 equiv of 2 and a small amount of 8 were returned. No higher molecular weight oligomers were detected under these conditions. The Al layer represented a 94.3% conversion of the theoretical (1 equiv).

The ratio of 15 to 16 was reversed (28:69) when the reaction was conducted with a 1:1:4:2 mole ratio of 14 and 2 with NaH and water for 6 h (red). About 3% of 14 was returned in this reaction.

Nitrobenzene (17), 2, and NaOH. 17 (0.369 g, 3.0 mmol) and 2 (1.908 g, 9.0 mmol) were dissolved in 25 mL of DMSO with NaOH (1.08 g, 27.0 mmol) and stirred for 5 h. The blue solution became dark orange within 1 h. Analysis of the neutral indicated a 42.4% yield of *N*-benzoylaniline (18), a sizeable amount of deoxybenzoin, and other compounds. PLC isolated 215 mg (36.4%) of 18, mp 162.5–163.5 °C (cyclohexane). No starting material, 17, was returned.

The original acidified water was made basic and extracted with ether. The ether was dried with Na_2SO_4 and evaporated to afford 140 mg of a yellow oil. GC/MS and FTIR analysis showed this oil to consist of mainly azoxybenzene (20, 102 mg, 0.515 mmol) and aniline (19, 18.8 mg, 0.2 mmol). These amounts correspond to yields of 34% and 6.7%, respectively.

9-Benzalfluorene (21), 2, and NaOH. 21 (1.27 g, 5.0 mmol) and 2 (1.06 g, 5.0 mmol) were dissolved in 25 mL of DMSO. NaOH (0.50 g, 12.5 mmol) was added and stirred for 6.5 h before workup (dark green). LC and GC/MS analysis of the neutral layer showed about 8.5% conversion of 21 to 9-benzylfluorene (22). Fractional recrystallization (EtOH) of a similar reaction gave 22; 5.1% of mp 132.5–134.5 °C (lit.[19] mp 134–5 °C).

9-Benzalfluorene (21), 2, NaOH, and H_2O. NaH (0.750 g of 80% in oil, 25.0 mmol) was washed under N_2 with hexanes. DMSO containing H_2O (0.270 g, 15.0 mmol) was added and stirred until the evolution of hydrogen began to subside. 21 (1.27 g, 5.0 mmol) and 2 (1.06 g, 5.0 mmol) were added with another 20 mL of DMSO and the mixture stirred for 6.5 h (dark red). Upon workup, it was necessary to filter a white precipitate that was poorly soluble in ether. This solid (0.713 g, 55.9%) was the crude hydrodimer 1,2-diphenyl-1,2-bis(9-fluorenyl)ethane (23), mp 305–315 °C (lit.[19] mp 310–313 or 319–320 °C). Recrystallization from anisole gave mp 310–313 °C (fast).

Concentration of the ether and trituration with $CHCl_3$ gave additional 23 (205 mg, 16.1%), mp 307–320 °C. LC and GC/MS analysis of the remains of the neutral layer indicated at 11.6% return of starting material and 5.9% of dihydro 22 in addition to another ~10% of 23.

The Al layer weighed 536 mg (2.35 mmol), which closely agrees with the amount of reduction shown by 82% of dimer 23 (2.05 mmol) and 6% of 22 (0.3 mmol).

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A New Three-Carbon Homologating Agent for Synthesis of γ-Keto Aldehydes

Xiyan Lu,* Cheng Guo, and Dawei Ma

Shanghai Institute of Organic Chemistry, Academia Sinica,
345 Lingling Lu, Shanghai 200032, China

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Homologation of aldehydes by three carbons is a process of considerable synthetic interest.[1,2] γ-Keto aldehydes are widely used in organic synthesis, especially as intermediates for the preparation of cyclopentenones.[3] A number of syntheses of γ-keto aldehydes with three-carbon homologating agents have been reported.[4-11] Most of these

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