Synthesis of Symmetrically and Unsymmetrically Substituted α-Diones from Organometallic Reagents and 1,4-Dialkylpiperazine-2,3-diones

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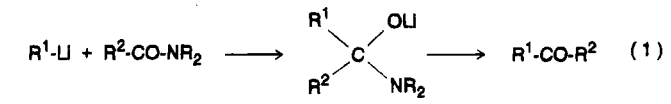
Received March 10, 1994®

The reaction of an equimolar mixture of *N,N'*-dialkylethylenediamines and diethyl oxalate in diethyl ether or 2-propanol leads to 1,4-dialkylpiperazine-2,3-diones. As cyclic and nearly planar tetraalkyl oxamides, these compounds are able to react with 2 equiv of organolithium or Grignard compounds to form, after hydrolysis, symmetrically substituted α-diones in excellent yields. The sequential addition of 1 equiv each of two different organolithium compounds affords unsymmetrically substituted α-diones when the more soluble longer chain dialkyl derivatives of piperazine-2,3-dione are employed. The dialkylethylenediamines can conveniently be recovered and recycled to the 1,4-dialkylpiperazine-2,3-diones in good yields.

Introduction

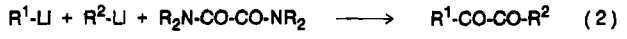
We wish to present details about a simple, high-yield, two-step synthesis of symmetrically substituted α-diones[1] and about how it can be extended to the preparation of unsymmetrically substituted α-diones (Scheme 1).

The method is based on the well-known[2] synthesis of aldehydes and ketones using dialkylamides and Grignard or organolithium reagents (eq 1), in which the stability



(1)

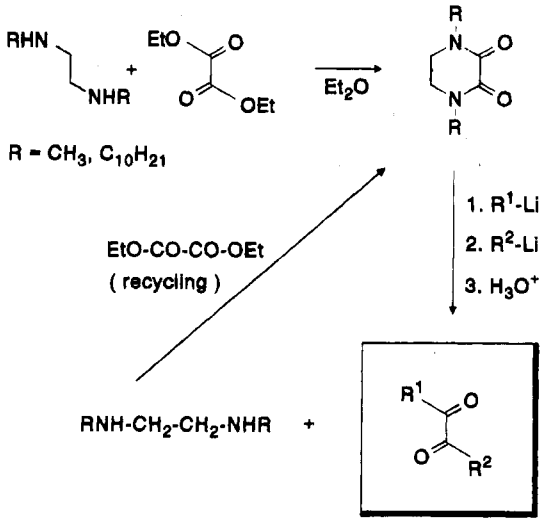
of the primary addition product is crucial for the success of the reaction: because the carbonyl product only forms upon hydrolysis, multiple additions of RLi or RMgBr (to lead to carbinols, as usually found in the reactions with esters) do not occur. It would therefore seem reasonable to expect that the addition of organolithium reagents to tetrasubstituted oxamides would lead to α-diketones (eq 2). The simplicity of this idea would seem to guarantee that it cannot be new, especially since α-diones are valuable synthetic intermediates.[3] Although several other more or less general syntheses of α-diones are known,[4] the reaction of eq 2 does not seem to have been realized to date.



(2)

There are two reasons why this reaction does not hold much promise as a practical synthesis: (1) most tetraalkyl oxamides are inconvenient to prepare,[5] (2) a fatal flaw (*vide infra*) of the above idea is that substituted oxamides do not react with organolithium compounds to form α-diones. In spite of this, we are able to report two convenient reactions: one leads to cyclic tetraalkyl oxamides in the simplest possible way and the other uses the reaction of these cyclic oxamides with organometallic reagents to produce symmetrically and unsymmetrically substituted α-diones in high yields.

Scheme 1. α-Diketone Syntheses via 1,4-Dialkylpiperazine-2,3-diones



Tetraalkyl Oxamides: Synthesis and Reactions. Tertiary amides usually are prepared by reacting dialkyl- or arylalkylamines with either an acid chloride or an ester. In the synthesis of tetrasubstituted oxamides, both of these reactions are inefficient, although ammonia and primary amines react as expected. The reaction of secondary amines with oxalyl chloride gives rather erratic results[5a] and occasionally leads to ureas as products of a decarbonylation reaction. The synthesis of

® Abstract published in *Advance ACS Abstracts,* July 15, 1994.

(1) A preliminary account on the synthesis of symmetrically substituted α-diones has been published: Mueller-Westerhoff, U. T.; Zhou, M. *Tetrahedron Lett.* **1993**, *34*, 571.

(2) (a) Wakefield, B. J. *Organolithium Methods*; Academic Press: New York, 1988. Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon: Oxford, 1974. (b) *Houben-Weyl Methoden der Organischen Chemie*; Thieme Verlag: Stuttgart, 1974; (4th ed.,) Vol. XIII/1. (c) Schlosser, M. *Polare Organometalle*; Springer Verlag: Berlin, 1973.

(3) Krongauz, E. S. *Russ. Chem. Rev.* **1977**, *46*, 1.

(4) (a) Tschugaeff, L. *Chem. Ber.* **1907**, *40*, 186–187. (b) Girard, P.; Couffignal, R.; Kagan, H. B. *Tetrahedron Lett.* **1981** *22*, 3959. See also: Collin, J.; Dallemer, F.; Namy, J.-L.; Kagan H. B. *Tetrahedron Lett.* **1984**, *25*, 2869. Soupper, J.; Namy, J.-L.; Kagan, H. B. *Tetrahedron Lett.* **1989**, *30*, 7407. Collin, J.; Namy, J.-L.; Dallemer, F.; Kagan H. B. *J. Org. Chem.* **1991**, *56*, 3118. (c) Braun, W. *Ger. Pat.* 913 891 (June 21, 1954); *Chem. Abstr.* **1956**, *52*, 14691f. (d) Comins, D. L. *Synlett* **1992**, 615. (e) Sibi, M. P.; Sharma, R.; Paulson, K. L. *Tetrahedron Lett.* **1992**, *33*, 1941. (f) Olah, G. A.; Wu, A.-H. *J. Org. Chem.* **1991**, *56*, 902–904.

(5) (a) Armbrecht, B. H.; Rice, L. M.; Grogan, C. H.; Reid, E. E. *J. Am. Chem. Soc.* **1953**, *75*, 4829. (b) Wilson, J. D.; Weingarten, H. *Can. J. Chem.* **1970**, *48*, 983.

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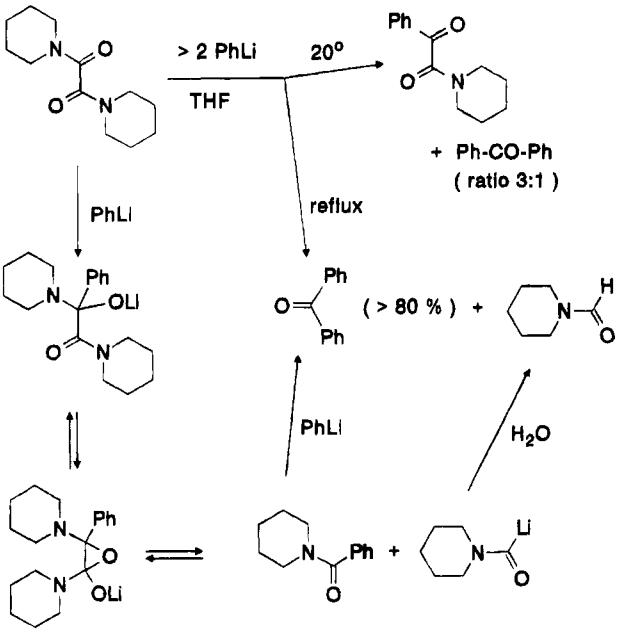
Scheme 2. Reactions of 1,1′-Oxalyldipiperidine with Phenyllithium

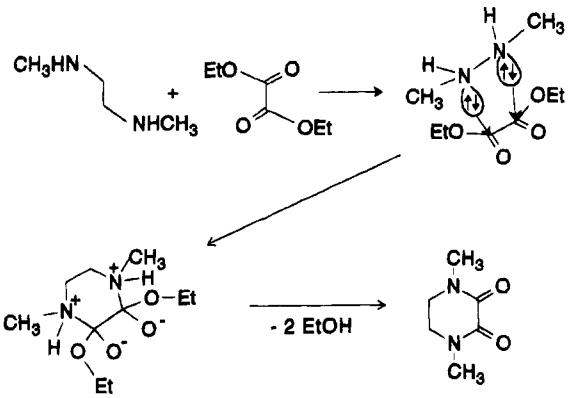


amides from esters and secondary amines fails in the case of oxamides, because it only leads to the half-reacted ester amides.[6] The only exception is the reaction of diethyl oxalate with 2 equiv of piperidine at reflux: as discovered over 100 years ago,[7,8] piperidine is able to react twice with the diester to give the bis-amide (1,1′-oxalyldipiperidine) after several hours of heating without a solvent. Removal of ethanol by evaporation gradually shifts the equilibrium to the diamide.[9]

In a short paper[4a] on the synthesis of α-diketones from 1,3-diphenyl-2-methylideneimidazolidine-4,5-dione, which comes closest to the work reported here, Tchugaeff in 1907 mentioned his intentions to treat the above oxalyldipiperidine with Grignard reagents to prepare α-diones (essentially proposing a reaction according to eq 2) but the results were never published, and neither have other publications relating to this idea appeared. We have found that oxalic dipiperidide is indeed useless for the synthesis of α-diones. For example, in the room-temperature reaction of this diamide either with stoichiometric amounts or with excess (up to 5 equiv) phenyllithium, the half-reacted keto amide (1′-piperidiyl-phenylethanedione) was formed together with traces of benzil and significant amounts of benzophenone. Extended reaction times (5 h) or elevated temperatures (reflux) led to benzophenone as the only isolated product (84% yield). Evidently, the product of the first addition of phenyllithium does not allow a second addition to complete the reaction in the desired direction.[10]

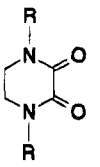
We speculate (Scheme 2) that the primary addition product can exist as an epoxide, which is unreactive to PhLi but equilibrates with benzoyl piperidine and a carbamoyllithium species. Benzoylpiperidine then reacts with PhLi in the normal way to form, after hydrolysis, benzophenone. The piperidionyllithium hydrolyzes to *N*-formylpiperidine, which was shown to be present in the aqueous layer. A similarly discouraging result was obtained when BuLi was used in this reaction. Although we have not determined the precise reaction details, these results make it clear that tetraalkyl oxamides do not have any value in the synthesis of α-diones. More successful are the reactions of *N,N′*-dimethoxy-*N,N′*-dimethyl oxamide with organometallic reagents, for which α-dione yields between 17 and 86% have been reported.[4e] The keto amides are byproducts (4–48%) in this case as well.

Scheme 3. Concerted Mechanism of DMPD Formation



Results and Discussion

Synthesis of DMPD. The cyclic oxamide **1** (1,4-dimethylpiperazine-2,3-dione, DMPD) was obtained by reacting equimolar amounts of *N,N′*-dimethylethylenediamine and diethyl oxalate in ether or 2-propanol as colorless crystals, which precipitated from the reaction medium in excellent (>90% of purified product) yield. No polymers or oligomers were formed.



1: R = CH_3 ("DMPD")

2: R = C_4H_9

3: R = $C_{10}H_{21}$ ("DDPD")

This reaction could result from a concerted, pericyclic reaction of a charge-transfer complex between the diamine and the diester, which preorients the reactants in their *cis* conformation and allows the simultaneous nucleophilic attack on the carbonyl carbon atoms to form the six-membered ring and ultimately of DMPD (Scheme 3). We favor this mechanism over a stepwise one because simple dialkylamines do not form tetraalkyl oxamides under these conditions. However, the entropy change in the formation of the cyclic product may indeed allow a stepwise reaction path in this case. It is of interest in this context that *N,N′*-dimethyl-*o*-phenylenediamine also reacts with diethyl oxalate under mild conditions, to form 1,2,3,4-tetrahydro-1,4-dimethyl-2,3-dioxoquinoxaline.[11] Experiments to elucidate the mechanism of DMPD formation have not provided a clear answer.

This reaction was first carried out in 1974, in ignorance on our part of the fact that diethyl oxalate does not form

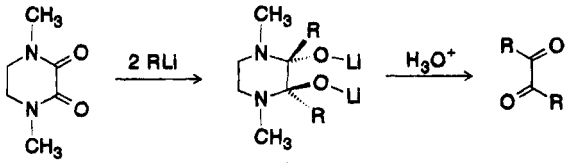
(6) A. W. v. Hofmann prepared the half-amide Et_2N—CO—CO—OEt in the reaction of the diethyl ester and diethyl amine: Hofmann, A. W. *J. Chem. Soc.* **1861**, 495; *Chem. Ber.* **1870**, *3*, 776.
(7) Wallach, O. *Liebigs Ann. Chem.* **1882**, *214*, 278.
(8) Schotten, C. *Chem. Ber.* **1882**, *15*, 421.
(9) Assistance by Daisy Githinji in reinvestigating this reaction is acknowledged.
(10) The formation of an aroyl carboxamide has previously been reported in the reaction of an aryllithium compound with tetramethyl oxamide: Campaigne, E.; Rogers, R. B. *J. Heterocycl. Chem.* **1973**, *10*, 297.
(11) Cheeseman, G. W. H. *J. Chem. Soc.* **1955**, 1804.

Table 1. Typical Reactions of DMPD with Organometallic Reagents

entry	organometallic reagent	conditions[a]	product	yield[b] (%)
1	C_6H_5Li	THF/30/20	Ph-CO-CO-Ph	95
2	C_6H_5MgBr	THF/60/20	Ph-CO-CO-Ph	84
3	C_4H_9Li	Ether/30/20	Bu-CO-CO-Bu	92
4	n-$C_{10}H_{21}MgBr$	THF/60/20	decyl-CO-CO-decyl	70
5	p-Jul-Li[c]	THF/60/−78 → 20	p-Jul-CO-CO-Jul(p)	83
6	2-naphthyl-Li	THF/60/−78 → 20	2-naphthyl-CO-CO-naphthyl(−2)	91
7	4-anisyl-Li	THF/60/−78 → 20	4-anisyl-CO-CO-anisyl(−4)	85[d]
8	CpFeCp-Li	THF/90/−78 → 20	CpFeCp-CO-CO-CpFeCp	85
9	CpRuCp-Li	THF/60/0 → 20	CpRuCp-CO-CO-CpRuCp	40[e]
10	1. C_6H_5Li (1 equiv) 2. C_4H_9Li (1 equiv)	THF/60/+ 30/20	Ph-CO-CO-Bu	20[f]

[a] Reaction conditions are given as solvent/reaction time (min)/temperature (°C). [b] Yields are based on recrystallized or distilled pure products, with DMPD as the limiting reagent. [c] Julolidinyl (abbreviated Jul) is 2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizinyl. [d] Lithioanisole was prepared from bromoanisole and BuLi; unreacted BuLi was not removed and the product contained 9% of p-CH_3O—C_6H_4—CO—CO—C_4H_9. [e] Dithioruthenocene contains significant amounts of 1,1′-dilithioruthenocene; a major product of this reaction therefore is CpRuCp—CO—CO—CpRuCp—CO—CO—CpRuCp. [f] The symmetrical diones Ph—CO—CO—Ph (40%) and Bu—CO—CO—Bu (30%) are the major products.

Scheme 4. Synthesis of α-Diones from DMPD



diamides in the reaction with secondary amines.[12] Meanwhile, DMPD and seven-membered analogs have also been obtained[13] in lower yield by similar reactions in benzene under reflux. We have also tested the seven-membered-ring analog for its suitability in forming α-diones: it does react similarly to DMPD and produces α-diones in good yields. Nevertheless, the ease with which DMPD can be prepared makes it a much more desirable synthon for α-diones.

Reactions of DMPD with Organometallics: α-Dione Syntheses. In spite of the fact that 1,1′-oxalyldipiperidine does not react in an analogous way, we expected the reaction of DMPD with 2 equiv of an organolithium or Grignard reagent to provide a general synthetic method for α-diones (Scheme 4). The required double addition of the organometallic reagent should be more probable than in the case of oxalyl dipiperidine, because (a) the addition to DMPD would preferably occur in the sterically more favored trans orientation to the fairly rigid six-membered ring and (b) the cyclic structure of DMPD should help prevent the formation of an epoxide.

When phenyllithium was reacted with DMPD in THF at room temperature, a 95% yield of pure benzil was obtained. To test the generality of this synthesis, similar reactions according to Scheme 3 were carried out with several different organometallic compounds. The results are summarized in Table 1. Reactions in THF, in which DMPD is slightly more soluble than in ether, appeared to be faster and to lead to slightly higher yields. Particularly noteworthy are the entries on diferrocenylethane-1,2-dione (no. 8) and bis(julolidinyl)ethane-1,2-dione (no. 5). These two compounds are not easily accessible by any of the standard syntheses of α-diones: in the ferrocene case, oxidation of 1,2-diferrocenylethane is an unreliable process,[14] and it is a well-known fact that Friedel–Crafts reactions, such as the reaction of julolidine with oxalyl chloride (in methylene chloride or carbon disulfide) produces the bis(julolidinyl)ethane-1,2-dione only in low yields.[15] That we were able to obtain both of these compounds in extremely good yields shows the advantage of the new method.

Synthesis of Unsymmetrically Substituted α-Diones. The sequential addition of two different organolithium species should lead to unsymmetrically substituted α-diones. Slow addition of 1 equiv of PhLi to a partial suspension of DMPD in THF, followed by addition of 1 equiv of BuLi, was expected to lead to 1-phenylhexane-1,2-dione (entry no. in 10 in Table 1). However, the reaction was not nearly as clean as the previous ones and only a low yield of the desired product was obtained. The main products were benzil and decane-5,6-dione. Because DMPD is only sparingly soluble in aprotic solvents at room temperature, the initial reaction is heterogeneous and even a very slow addition of the organometallic reagent cannot avoid the double addition of PhLi to DMPD. In the above case, this leads to the preferred formation (40%) of benzil. A smaller amount of monoadduct is formed as well which, upon addition of BuLi, produces the unsymmetrically substituted α-dione (in 20% yield). The remainder of the unreacted DMPD is consumed by BuLi to form the symmetrically substituted Bu—CO—CO—Bu (30%). This result implies that this method should be more generally applicable, but that our heterogeneous reaction conditions were unsuitable. Unfortunately, DMPD is poorly soluble in all solvents which are useful for reactions with organolithium or Grignard reagents. A more soluble DMPD derivative would allow these reactions to be homogeneous and would therefore be more likely to produce unsymmetrically substituted α-diones in yields approaching those of the symmetrical ones.

Long-Chain DMPD Analogs: Synthesis and Reactions. To obtain a more soluble DMPD-like reagent, we prepared two long-chain N,N'-dialkylpiperazine-2,3-

(12) The original synthesis of 1 was buried as an unimportant side result in a report on the synthesis of dithiolene complexes. The reaction of 1 with P_4S_{10} led to the dithione, which was used in the synthesis of dithiolene complexes: Nazzal, A.; Lane, R. W.; Mayerle, J. J.; Mueller-Westerhoff, U. T. *United States NTIS, Final Report USARO* **1978**, *78*, 137. See also: Mueller-Westerhoff, U. T.; Vance, B. Chapter 16.5. in *Comprehensive Coordination Chemistry*, Wilkinson, G., Ed., Pergamon Press: Oxford, 1987.

(13) Isaksson, R.; Liljeford, T.; Sandström, J. *J. Chem. Res. (S)* **1981**, *43*; *J. Chem. Res. (M)* **1981**, 664–682.

(14) Nesmeyanov, A. N.; Perevalova, E. G.; Tsiskaridze, T. T. *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1966**, 2136 (*Chem. Abstr.* **1967**, *66*, 85846r). Gmelin's *Handbuch der Anorganischen Chemie*, Vol. 41, *Eisen-Organische Verbindungen*, Part A6, 80–87.

(15) Mueller-Westerhoff, U. T.; Vance, B.; Yoon, D. I. *Tetrahedron* **1991**, *47*, 909.

Table 2. Synthesis of Unsymmetrically Substituted α-Diones from DDPD[a]

entry	organometallic reagent (equiv)	conditions[b]	product	yield[c] (%)
1	1. C_4H_9-Li (1) 2. C_6H_5-Li (1)	hexane/60 + 60/66	Ph-CO-CO-Bu	78[d]
2	1. C_6H_5-Li (1) 2. Jul-Li (1)	THF/60 + 60/0	Ph-CO-CO-Jul	75[e]
3	1. C_6H_5-Li (1) 2. 2-naphthyl-Li (1)	THF/60 + 60/0	Ph-CO-CO-naphthyl(−2)	74[f]
4	1. C_6H_5-Li (1) 2. 4-anisyl-Li (1)	THF/60 + 60/0	Ph-CO-CO-anisyl(−4)	65[g]

[a] DDPD is 1,4-didecylpiperazine-2,3-dione (**3**). [b] Reaction conditions are given as solvent/reaction time (min)/temperature (°C). [c] Yields are based on recrystallized or distilled pure products. [d] The symmetrical dione Bu-CO-CO-Bu was isolated in 8% yield. [e] Julodinyl (abbreviated Jul) is 2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizinyl. The symmetrical dione Jul-CO-CO-Jul was isolated in 10% yield. [f] Bis(2-naphthyl)ethanedione was isolated in 7% yield. [g] Bis(4-anisyl)ethanedione was obtained in 15% yield; 5% of benzil was isolated.

diones, the dibutyl compound **2** and its didecyl analog **3** (DDPD). These two were chosen because we expected to see some differences in solubility and in the ease with which they could be crystallized and purified. The syntheses followed the route established for DMPD itself. The necessary *N,N'*-dialkylethylenediamines were obtained from 1,2-dibromoethane and the two alkylamines, respectively.[16] Their reactions with diethyl oxalate led to **2** and **3** in good yields. Both are soluble in ether and THF. The solubility of **2** at room temperature in hexane or heptane is limited, but **3** dissolves in these solvents at elevated temperatures and can be easily purified by recrystallization from heptane.

As expected, reaction of either **2** or **3** with PhLi in ether again produced benzil in excellent yield. To determine whether or not the soluble DMPD derivatives would allow us to prepare an unsymmetrically substituted α-diketone, 1 equiv of BuLi was very slowly added to a solution of DDPD (**3**) in hexane at reflux; after 1 h, 1 equiv of PhLi was added, and the solution was allowed to cool. Hydrolysis and purification by column chromatography and vacuum distillation produced 1-phenylhexane-1,2-dione in 78% yield and only minor amounts of the symmetrical α-diones.

Similarly, the sequential reaction of other pairs of organolithium reagents with DDPD led to the formation of other unsymmetrically substituted α-diones as the major product. These results are summarized in Table 2. In the workup of the above reactions, the *N,N'*-didecylethylendiamine can be conveniently separated and recycled to DDPD. Upon acidification of the reaction mixture with HCl (or NH_4Cl), the diamine hydrochloride precipitates and can be isolated and reacted with diethyl oxalate in the presence of a base. This recycling aspect makes this reaction particularly attractive in environmental respects.

Summary

For the direct synthesis of symmetrical α-diones from organometallic reagents, DMPD seems to be the most useful reagent to date. It is simply and cheaply obtainable and reacts to form α-diones in excellent yields. Its poor solubility in aprotic solvent leads to heterogeneity of its reactions with organometallic reagents. Whereas this is of no consequence in the synthesis of symmetrically substituted α-diones, it is a problem for the synthesis of unsymmetrically substituted α-diones. Even very slow addition of the first organometallic reagent does not preclude the formation of the symmetrically substituted products as the major ones. To overcome these solubility problems in the preparation of unsymmetrically substituted α-diones, long-chain dialkyl analogs of DMPD can be employed. They are very soluble in THF, ether, and even in alkanes at elevated temperatures. This allows their sequential reactions with two different organometallic reagents to be carried out under homogeneous reaction conditions, which proved to be a prerequisite for these syntheses. The addition sequence seems unimportant as long as the solution of the first organometallic reagent is precisely titrated to guarantee a stoichiometric first addition step. Having at hand a choice of 1,4-dialkylpiperazine-2,3-dione intermediates, we are now able to carry out the synthesis of symmetrical and unsymmetrical α-diones with equal success. The long-chain ethylenediamines can easily be recycled to their respective DMPD derivatives. In view of this fact, the net result of the overall sequence of reactions (i.e.: EtO-CO-CO-OEt + R^1-Li + R^2Li → R^1-CO-CO-R^2 + 2LiOEt) represents an efficient conversion of diethyl oxalate to α-diones by an addition of organolithium compounds—a reaction which cannot be realized directly in any practical or effective manner.[17]

Experimental Section

General Methods. All reactions involving air- or moisture-sensitive reagents were carried out under a positive pressure of N_2. Reagents and solvents were used as received from commercial sources except for THF, which was distilled from sodium/benzophenone, and hexane, which was distilled from sodium. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ solution with 1% TMS as internal standard. Analytical TLC was carried out on Baker-Flex silica gel IB2-F plates. Preparative column chromatography was performed with silica gel (J. T. Baker, 60-200 mesh).

1,4-Dimethylpiperazine-2,3-dione (1, DMPD). To a stirred solution of *N,N'*-dimethylethylenediamine (10.0 mL, 8.3 g, 94 mmol) in 200 mL of anhydrous ether was added diethyl oxalate (12.7 mL, 13.7 g, 94 mmol) in one portion. After a few minutes white crystals began to precipitate. The mixture was stirred overnight. The product was filtered and washed with dry ether. Recrystallization from toluene produced 12.0 g (90%) of DMPD, mp 178−79 °C (lit.[13] mp 176−79 °C): ^{1}H NMR ($CDCl_3$) δ 3.09 (s, 6H), 3.59 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 157.4, 34.8, 46.0; MS *m/z* 142 (M^+), 114 (M - CO), 113.

1,4-Didecylpiperazine-2,3-dione (3, DDPD). *N,N'*-Didecylethylenediamine was prepared[16] from 1,2-dibromoethane (8.2 mL, 17.9 g, 9.52 mmol) and 4 equiv (77.0 mL, 61.1 g, 0.39 mol) of 1-decylamine in 95% EtOH at reflux for 12 h. The hydrobromide salt precipitated upon cooling and was filtered. Treatment of a suspension of this salt in CH_2Cl_2 with 1 N KOH gave the free amine. Recrystallization from 95% EtOH yielded

(16) Chamizo, J. A.; Lappert, M. F. *J. Org. Chem.* **1989**, *54*, 4684.

(17) An exception is the moderate yield (28%) synthesis of symmetrical dithienyl ethanediones from dimethyl oxalate and 2- or 3-thienyllithium at −78 °C: Nyberg, K. *Acta Chem. Scand.* **1969**, *23*, 1087.

22.5 g (60%) of the diamine as a white solid, mp 62–64 °C: ^{1}H NMR ($CDCl_3$) δ 2.72 (s, 4H), 2.59 (t, 4H), 1.75 (br, 2H), 1.48 (m, 4H), 1.26 (br, 28H), 0.88 (t, 6H); ^{13}C NMR ($CDCl_3$) δ 50.1, 49.6, 31.9, 30.2, 29.6, 29.6, 29.3, 27.4, 22.7, 14.1; MS *m/z* 339 ($M^+ - H$), 170 ($M^+/2$), 44.

1,4-Didecylpiperazine-2,3-dione (3, DDPD). A solution of *N,N'*-didecylethylenediamine[15] (5.0 g, 14.8 mmol) and diethyl oxalate (2.0 mL, 14.8 mmol) in 120 mL anhydrous ether was stirred at rt overnight. After removal of the solvent, the white solid was recrystallized from hexane to yield 5.5 g (94%) of DDPD, mp 114–116 °C: ^{1}H NMR ($CDCl_3$) δ 3.51 (s, 4H), 3.46 (t, 4H), 1.57 (m, 4H), 1.26 (br, 28H), 0.88 (t, 6H); ^{13}C NMR ($CDCl_3$) δ 157.3, 47.5, 47.5, 31.8, 29.5, 29.3, 29.3, 27.2, 26.6, 22.6, 14,1; MS *m/z* 394 (M^+), 295, 239, 184, 168, 113, 57.

Synthesis of Symmetrical α-Diones from DMPD: Benzil. To a suspension of DMPD (**1**, 2.13 g, 15.0 mmol) in 60 mL of dry THF was added 18.0 mL of PhLi (2.0 M in cyclohexane, 36.0 mmol) by a syringe. After 30 min of stirring at rt, the solution was hydrolyzed with 100 mL of 10% HCl and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated. The yellow residue was chromatographed on silica gel, first with hexane to remove biphenyl (present in the phenyllithium solution) and then with hexane/CH_2Cl_2 (1:1) to elute the yellow band of the product. Recrystallization from heptane yielded 2.99 g (95%) pure benzil of mp 94–95 °C (lit.[18] mp 95 °C), identical by IR, ^{1}H NMR, ^{13}C NMR, and MS with an authentic sample.

Synthesis of Unsymmetrical α-Diones from DDPD: Julolidinylphenylethanedione. *p*-Bromojulolidine[19] (3.2 g, 12.7 mmol) was reacted with butyllithium (9.0 mL of a 1.40 M solution in hexane, 12.6 mmol) at −78 °C in 40 mL of dry THF. The tan suspension was stirred for 2 h at −78 °C. During this time, a solution of DDPD (3.45 g, 8.75 mmol) in 70 mL of dry THF was cooled to 0 °C and 5.0 mL of PhLi (1.75 M in cyclohexane/ether, 8.75 mmol) was added very slowly (40 min). The mixture was stirred for 1 h. The cold slurry of lithiojulolidine was transferred under positive nitrogen pressure through a cannula to the DDPD/PhLi reaction mixture to form a brownish solution which was stirred for 1 h at 0 °C and for 1 h at rt. The product solution was hydrolyzed with 200 mL of saturated NH_4Cl solution and extracted three times with CH_2Cl_2. The colorless solid produced at this stage was filtered and dried *in vacuo* to give 2.96 g (90%) of the *N,N'*-didecylethylenediamine HCl salt. The free diamine was recovered by extraction with CH_2Cl_2 from a suspension of the salt in 1 N KOH and was reacted with diethyl oxalate to DDPD (2.9 g, overall recycling yield 85%). The yellow organic filtrate of the previous step was evaporated to dryness and chromatographed on silica gel with CH_2Cl_2. The first band afforded 2.0 g (75%) of yellow crystals, mp 130–32 °C, which were identified as 1-julolidinylphenylethanedione. A second yellow band was eluted with CH_2Cl_2 and 1% ether and was identified as containing dijulolidinylethanedione (0.35 g, 10%), identical with an authentic sample (Table 1, entry 5). 1-Julolidinylphenylethanedione: ^{1}H NMR ($CDCl_3$) δ 7.98–7.42 (m, 5H), 7.38 (s, 2H), 3.26 (t, 4H), 2.66 (t, 4H), 1.90 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 195.8, 192.0, 148.2, 134.0, 133.7, 129.7, 129.3, 128.6, 120.2, 119.2, 49.9, 27.5, 20.9; MS *m/z* 305 (M^+), 200 (Jul-CO^+), 172, 77 (Ph^+).

Diferrocenylethane-1,2-dione. *t*-BuLi in pentane (15.0 mL, 1.575 M, 23.6 mmol) was added dropwise to a solution of ferrocene (5.07 g, 27.3 mmol) in 50 mL THF at 0 °C.[20] After 15 min of stirring at 0 °C, dry hexane (60 mL) was slowly added. The precipitated orange solid of lithioferrocene was allowed to settle, the supernatant was removed through a cannula under positive N_2 pressure, and the residue was suspended in 25 mL of hexane with stirring. Stirring was stopped, the solid was allowed to settle, and the hexane was removed via cannula. Ferrocene (2.89 g) was recovered from the hydrolyzed filtrates. Dry hexane (25 mL) was added to the solid, the suspension was cooled to −78 °C, and 70 mL of dry THF were added. DMPD (0.30 g, 2.1 mmol) was then added in one portion and the mixture was allowed to warm to room temperature. After 3 h the mixture was hydrolyzed with saturated NH_4Cl solution and extracted with CH_2Cl_2. Evaporation of the organic phase led to a red residue which was chromatographed on silica gel with CH_2Cl_2 as eluent. After ferrocene (1.34 g) was collected, the second band afforded 0.76 g (85%, based on DMPD) of diferrocenylethane-1,2-dione as a red-purple solid, mp 194–96 °C (lit.[21] mp 193.5–195.5 °C), identical by ^{1}H NMR, ^{13}C NMR, and MS with an authentic sample.[14]

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