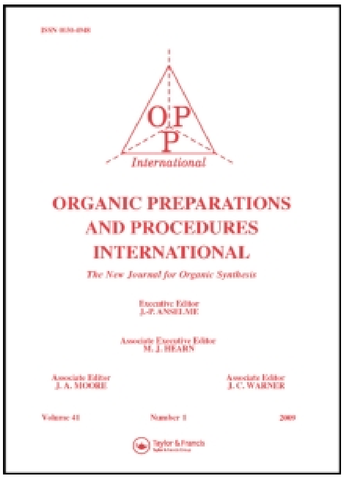


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

SYNTHESIS OF DIIMINES FROM 1,2-DICARBONYL COMPOUNDS BY DIRECT CATALYZED CONDENSATION

D. Armesto[a]; P. Bosch[a]; M. G. Gallego[a]; J. F. Martin[a]; M. J. Ortiz[a]; R. Perez-Ossorio[a]; A. Ramos[a]
[a] Departamento de Quimica Organica, Facultad de Química, Universidad Complutense, Madrid, SPAIN

To cite this Article Armesto, D. , Bosch, P. , Gallego, M. G. , Martin, J. F. , Ortiz, M. J. , Perez-Ossorio, R. and Ramos, A.(1987) 'SYNTHESIS OF DIIMINES FROM 1,2-DICARBONYL COMPOUNDS BY DIRECT CATALYZED CONDENSATION', Organic Preparations and Procedures International, 19: 2, 181 — 186

To link to this Article: DOI: 10.1080/00304948709356185

URL: http://dx.doi.org/10.1080/00304948709356185

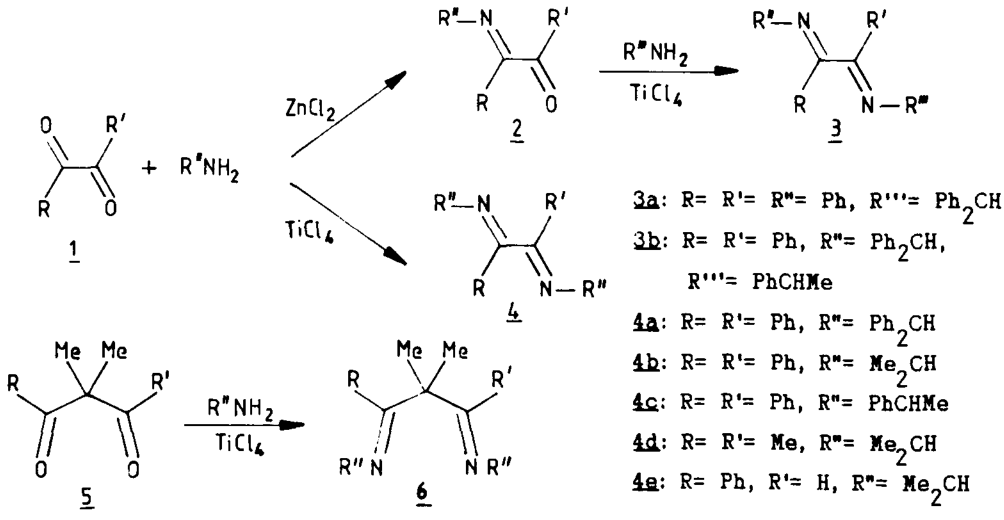
ORGANIC PREPARATIONS AND PROCEDURES INT. 19(2-3), 181-186 (1987)

SYNTHESIS OF DIIMINES FROM 1,2-DICARBONYL COMPOUNDS BY DIRECT CATALYZED CONDENSATION

D. Armesto,* P. Bosch, M. G. Gallego, J. F. Martin,
M. J. Ortiz, R. Perez-Ossorio and A. Ramos

Departamento de Química Orgánica, Facultad de Química,
Universidad Complutense, 28040-Madrid, SPAIN

Diimines have been used as precursors to some heterocyclic compounds such as imidazolines[1] and pyrimidines,[2] as well as bidentate ligands for a variety of metals.[3] There are only a few routes to the synthesis of diimines of 1,2-dicarbonyl compounds. The direct method by reacting the carbonyl compound with amine succeeds only with reactive carbonyl groups as in biacetyl[4] and fails with benzil even under forcing conditions.[5] Alternative methods such as the reaction of Grignard reagents with isonitriles,[6] cyanide-catalyzed condensation of anils,[7] and mercuric acetate catalyzed addition of



1 2 3 4 5 6

3a: R= R'= R"= Ph, R'''= Ph_2CH

3b: R= R'= Ph, R"= Ph_2CH, R'''= PhCHMe

4a: R= R'= Ph, R"= Ph_2CH

4b: R= R'= Ph, R"= Me_2CH

4c: R= R'= Ph, R"= PhCHMe

4d: R= R'= Me, R"= Me_2CH

4e: R= Ph, R'= H, R"= Me_2CH

6a: R= R'= R"= Ph **6b**: R= R'= Ph, R"= $PhCH_2$

amines to propargyl alcohol[8] have been reported. None of these methods is general; they have limited flexibility for varying substituents, and yield diimines with identical substitution on the nitrogens. The synthesis of the N-unsubstituted diimine of benzil has also been reported[1] using the direct reaction of sodium bis(trimethylsilyl)amide with benzil. 1,3-Diimines are even less common; since direct attack of amine on a 1,3-diketone fails, the only synthetic approach is the addition of anions of ketimines to nitriles.[9]

TABLE I. Yields, Melting Points and Elemental Analysis of **3**, **4** and **6**

Cmpd	Yield[a] (%)	mp (°C)	Formula	Elemental Analysis Calcd. (Found) C	H	N
3a	42	101-102	$C_{33}H_{26}N_2$	88.00 (87.98)	5.78 (5.60)	6.22 (6.00)
3b	47	146-148	$C_{35}H_{30}N_2$	87.65 (87.86)	6.40 (6.28)	5.70 (5.86)
4a	64	176-178	$C_{40}H_{32}N_2$	88.82 (89.20)	5.92 (5.97)	5.18 (5.07)
4b	63	68-73	$C_{20}H_{24}N_2$	82.19 (81.94)	8.22 (8.04)	9.59 (9.63)
4c	70	158-160	$C_{30}H_{28}N_2$	86.53 (86.39)	6.73 (6.52)	6.73 (6.61)
4d	93	b		c		
4e	77	72-75	$C_{14}H_{20}N_2$	77.77 (77.46)	9.25 (9.55)	12.96 (13.08)
6a	40	101-102	$C_{29}H_{26}N_2$	86.53 (86.24)	6.51 (6.68)	6.96 (6.82)
6b	27	61	$C_{31}H_{30}N_2$	86.47 (86.40)	7.02 (6.83)	6.51 (6.20)

a) Yields are for pure recrystallized products and are not optimized.
b) bp. 25°/0.1 mm Hg. c) The product was unstable and gave unreliable microanalytical data.

We now report a general synthetic procedure for the facile synthesis of 1,2 and 1,3-diimines involving reaction of the corresponding dicarbonyl compound with titanium (IV) chloride[10] in the presence of a large excess of an amine at room temperature for 2-4 days under an atmosphere of nitrogen. Work-up gives good to excellent yields of the corresponding 1,2- and 1,3-diimines **3**, **4** and **6** (Table I) whose spectral data are collected in Table II.

TABLE II. Spectral Data of 3, 4 and 6

Cmpd	IR[a] (cm^{-1})	^{1}H-NMR (δ) ($CDCl_3$)
3a	1615	5.6 (s, 1H, CH); 6.3-6.7 (m, 2H, aromatics); 7.1-7.5 (m, 19H, aromatics); 7.7-8.0 (m, 4H, aromatics).
3b	1610 1615	1.0 (d, 3H, CH_3); 4.3 (q, 1H, CH); 5.6 (s, 1H, CH); 6.9-8.0 (m, 25H, aromatics).
4a	1620	5.6 (s, 2H, CH); 6.9-8.0 (m, 30H, aromatics).
4b	1620	1.0 (d, 6H, $2CH_3$); 1.2 (d, 6H, $2CH_3$); 3.6 (m, 2H, 2CH); 7.2-7.6 (m, 6H, aromatics); 7.7-8.0 (m, 4H, aromatics).
4c	1620	1.0 (d, 3H, CH_3); 1.3 (d, 3H, CH_3); 4.1 (m, 1H, CH); 4.6 (m, 1H, CH), 6.8-8.0 (m, 20H, aromatics).
4d	1640	1.3 (d, 12H, $4CH_3$); 2.2 (s, 6H, $2CH_3$); 3.9 (m, 2H, 2CH).
4e	1630 1610	[b]1.0 (d, 12H, $4CH_3$); 3.4 (m, 2H, 2CH); 7.0-7.3 (m, 5H, aromatics); 7.8 (s, 1H, CH=).
6a	1630	1.6 (s, 6H, $2CH_3$); 6.5-7.2 (m, 20H, aromatics).
6b	1650	1.5 (s, 6H, $2CH_3$); 4.4 (s, 4H, $2CH_2$); 6.8-7.4 (m, 20H, aromatics)

a) As KBr pellets. b) In CCl_4

The use of biacetyl clearly demonstrates that the alkyl substituents in the carbonyl compound does not affect the condensation with the amine, and that the titanium (IV) chloride reaction is applicable even to reactive carbonyl compounds. The versatility of the titanium (IV) chloride approach is demonstrated by the synthesis of the unsymmetrically substituted diimines 3a and 3b. Only the monoimine 2 is formed by the $ZnCl_2$-catalyzed reaction of diphenylmethyl amine with benzil.[5] This monoimine 2 is resistant to further condensation except when titanium (IV) chloride is used as the catalyst and thus, can be reacted with aniline or phenylethylamine to yield the unsymmetrical diimines 3a and 3b.

Titanium (IV) chloride induced condensation of the 1,3-dicarbonyl compound 5 with aniline and benzylamine yielded the diimines 6a and 6b respectively. As far as we are aware, these are the only examples of 1,3-diimines. Previous reports of attempted synthesis of less substituted 1,3-diimines[2,11] indicate that formation of the enamines always occurred.

EXPERIMENTAL SECTION

Melting points were determined with a Buchi apparatus in capillary tubes and are uncorrected. The IR spectra were recorded on a Perkin-Elmer 257 and the ^{1}H-NMR spectra were measured with a Varian T-60A. A Varian MAT 711 was used for the mass spectra. Microanalysis were performed by the Centro Nacional de Química Orgánica del C.S.I.C. of Madrid.

N-Benzhydryl-1-benzoylbenzylidenimine (2).- This monoimine was prepared with slight modification of literature procedure.[5] A solution of benzil (8.0 g, 38 mmol) and benzhydrylamine (6.96 g, 38 mmol) was refluxed in toluene (100 ml) for 36 hours, in the presence of catalitic amounts of $ZnCl_2$, under conditions for azeotropic removal of water. Concentration of the resultant solution *in vacuo* give 9.5 g (66%) of an oily residue that was crystallized from ethanol to yield 8.9 g (63%) of white crystals, mp 131-132°C (lit.[5] 130-131°C).

General Procedure for the Preparation of Diimines.- A 250 ml three-necked round-bottomed flask, equipped with a magnetic stirring bar, a 100 ml pressure equalizing addition funnel with a septum, a nitrogen gas inlet tube and a reflux condenser, was charged with a solution of the diketone or the monoimine and the amine in 100 ml of benzene. The addition funnel was charged with 50 ml of benzene and the system was cooled to 0-5° using and ice-water bath. Titanium (IV) chloride was added *via* syringe to the addition funnel and the solution was added dropwise to the reaction flask over a period of about 30 min. After the addition was complete, the reaction mixture was stirred for 2-4 days at room temperature, then filtered, and the solvent and the excess of amine were removed under vacuum. The crude product was distilled at reduced pressure or crystallized. The quantities of reagents used in each case are given below.

1,2,3,5,5-Pentaphenyl-1,4-diaza-1,3-pentadiene (3a) from N-benzhydryl-1-benzoylbenzylideneimine (2) (2 g, 6 mmol), aniline (15 g, 150mmol) and titanium (IV) chloride (0.9 ml, 8 mmol); crystallized from ethanol to yield 1 g (42%). MS m/z (rel. intensity): 450 (<1) M^+, 373 (8), 360 (80), 181 (19), 180 (100), 77 (68); UV(EtOH) λ max 264 nm (ε 61250).

1,1,3,4,6-Pentaphenyl-2,5-diaza-2,4-heptadiene (3b) from N-benzhydryl-1-benzoylbenzylidenimine (2) (1.48 g, 4 mmol), 1-phenylethylamine (15 ml, 120 mmol), titanium (IV) chloride (1 ml, 9 mmol); crystallized from ethanol to yield 0.88 g (47%). MS m/z (rel. intensity): 478 (2) M^+, 373 (23), 312 (10), 311 (39), 167 (82), 165 (21), 152 (11), 105 (100).

1,1,3,4,6,6-Hexaphenyl-2,5-diaza-2,4-hexadiene (4a) from benzil (0.64 g, 3 mmol), benzhydrylamine (14 g, 77 mmol) and titanium (IV) chloride (0.5 ml, 5 mmol); crystallized from ethanol to yield 1.06 g (64%). MS m/z (rel. intensity): 540 (6) M^+, 373 (88), 271 (14), 269 (17), 167 (100), 152 (24).

2,7-Dimethyl-4,5-diphenyl-3,6-diaza-3,5-octadiene (4b) from benzil (2 g, 9.5 mmol), isopropylamine (33 ml, 380 mmol) and titanium (IV) chloride (1.5 ml, 15 mmol); crystallized from ethanol to yield 1.7 g (63%). MS: m/z (rel. intensity): 292 (<1) M^+, 277 (23), 206 (6), 163 (7), 147 (23), 105 (15), 104 (100), 77 (12); UV(EtOH): λ max 248 nm (ε 49166).

2,4,5,7-Tetraphenyl-3,6-diaza-3,5-octadiene (4c) from benzil (0.73 g, 3 mmol), 1 -phenylethylamine, (12 ml, 104 mmol) and titanium (IV) chloride (0.6 ml, 5.1 mmol); crystallized from ethanol to yield 1.0 g (70%). MS m/z (rel. intensity): 374 (2) (M^+-42), 360 (18), 180 (100), 104 (5), 77 (33); UV(EtOH) λ max 252 (ε 7500).

2,4,5,7-Tetramethyl-3,6-diaza-3,5-octadiene (4d) from biacetyl (1g, 11.6 mmol), isopropylamine (19.7, 232 mmol) and titanium (IV) chloride (1.53 ml, 14 mmol) to yield 1.8 g (93%) of a colorless oil. MS m/z (rel. intensity): 168 (2) M^+,153 (90), 125 (6), 111 (44), 101 (24), 84 (82), 70 (13), 42 (100).

2,7-Dimethyl-4-phenyl-3,6-diaza-3,5-octadiene (4e) from phenylglyoxal monohydrate (2 g, 13.1 mmol), isopropylamine (22.5 ml, 263 mmol) and titanium (IV) chloride (1.7 ml, 15.7 mmol) to yield 2.2 g (77%); partial decomposition is observed in crystallization from ethanol or hexane. MS m/z (rel. intensity): 216 (1) M^+, 201 (54), 173 (3), 159 (22), 146 (8), 132 (3), 102 (100), 77 (13), 43 (16).

3,3-Dimethyl-1,2,4,5-tetraphenyl-1,5-diaza-1,4-pentadiene (6a) from 2,2-dimethyl-1,3-diphenyl-1,3-propanedione (4.2 g, 17 mmol), aniline (93 ml, 1 mol) and titanium (IV) chloride (6.7 ml, 60 mmol); crystallized from ethanol to yield 2.7 g (40%). MS m/z (rel. intensity): 402 (0.2) M^+, 387 (15), 181 (16), 180 (100), 105 (28), 77 (44).

4,4-Tetramethyl-1,3,5,7-tetraphenyl-2,6-diaza-2,5-heptadiene (6b) from 2,2-dimethyl-1,3-diphenyl-1,3-propanedione (1g, 4 mmol) benzylamine (26 ml, 0.24 mol) and titanium (IV) chloride (1.6 ml, 15 mmol); crystallized from ethanol to yield 0.46 g (27%). MS m/z (rel. intensity): 430 (0.5) M^+, 415 (27), 339 (46), 105 (4), 91 (100), 77 (5).

REFERENCES

1. G. Tuchtenhagen and K. Rühlmann, Ann., 711, 174 (1968).
2. H. Hoberg and J. Barluenga, Synthesis, 363 (1970).
3. H. Bock and H. Diek, Chem. Ber., 100, 228 (1967).
4. H. Dieck and J. Dietrich, ibid., 117, 694 (1984).
5. J. L. Garcia Ruano, M. A. Henao, D. Molina, R. Perez-Ossorio, and J. Plumet, An. Quim., 76C, 260 (1980); Chem. Abs., 95, 24130e (1981).
6. I. Ugi and U. Fetzer, Chem. Ber., 94, 2239 (1961).
7. J. S. Walia, J. Singh. M. S. Chattha, and M. Satyanakayana, Tetrahedron Lett., 195 (1969).
8. J. Barluenga, F. Aznar, and R. Liz, J. Chem. Soc., Perkin Trans. I, 1093 (1983).
9. H. Hoberg and J. Barluenga, Synthesis, 142 (1970).
10. I. Moretti and G. Torre, ibid., 141 (1970).
11. J. Barluenga, B. Olano, and S. Fustero, J. Org. Chem., 48, 2255 (1983).

(Received July 22, 1986; in revised form December 1, 1986)