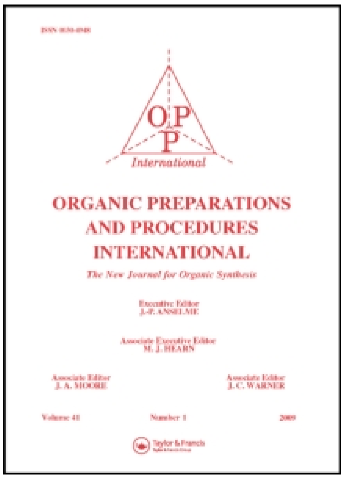

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THE PREPARATION OF SOME DIIMINES

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THE PREPARATION OF SOME DIIMINES

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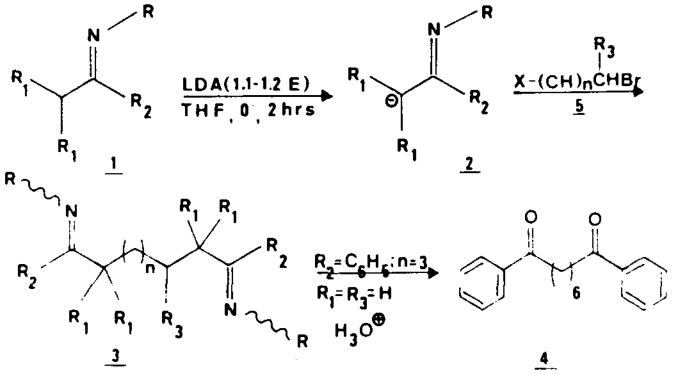
Imine anions react with a great variety of reagents often to form quite versatile products.[1] They can be used to form ω-halogenated aldehydes and dialdehydes[1-7] by reaction with ω,ω'-dihaloalkanes followed by hydrolysis. Nevertheless the intermediate ω-haloimines have never been isolated. During the study of the synthesis and the reactivity of ω-haloimines, we have now obtained a variety of diimines **3** by the reaction of imine anions **2** with ω,ω'-dihaloalkanes. Imine anions



a) R=*t*-Bu, $R_1=R_3=CH_3$, $R_2=H$; b) R=*c*-Hex, $R_1=R_3=CH_3$, $R_2=H$;
c) R=*i*-Pr, $R_1=R_3=CH_3$, $R_2=H$; d) R=*i*-Pr, $R_1=R_3=H$, $R_2=C_6H_5$;
e) R=*i*-Pr, $R_1=CH_3$, $R_2=R_3=H$; f) R=*t*-Bu, $R_1=CH_3$, $R_2=R_3=H$;
g) R=*t*-Bu, $R_1=CH_3$, $R_2=R_3=H$

2 can easily be generated by reaction of imines 1 with LDA (lithium diisopropylamide : 1.1-1.2 equivalents) in THF at 0° (2 hrs). Earlier findings[2,3] described the deprotonation of imines 1 with LDA at -60° but we found that the anions could also be generated at 0° without side-reactions. After addition of 0.5 equivalent of dihaloalkanes to the imine anions at 0° and after overnight stirring, the corresponding diimines 3 were isolated in 62-95 % yield. The results of the preparation of diimines 3 are summarized in Table 1.

TABLE 1. Preparation of Diimines 3[a]

Cmpd	n	LDA[b]	5	Yield of 3 (%)	bp (°C/mm Hg)
3a	2	1.1E	0.5E	62 %	97-103/0.7
3b	2	1.2E	0.5E	82 %	145-150/0.4
3c	2	1.2E	0.5E	75 %	-
3d	3	1.1E	0.5E	85 %	185-190/0.15
3e	3	1.1E	0.5E	95 %	82-85/0.40
3f	3	1.2E	1.1E	30 %[c]	82-90/0.10
3g	2	1.2E	1E	50 %[c]	85-87/0.05

a) X is Br except for 3f and 3g; yields are of distilled products (except 3c); diimines 3a, 3c, 3f and 3g gave correct nitrogen analyses.

b) E = equivalent

c) As a byproduct of the synthesis of ω-chloroimines; X=Cl.

Hexamethylphosphortriamide was used in one experiment but did not increase the yield of the diimine 3. Normally 0.50 equivalent of the dihaloalkane was used except for 3f and 3g where the diimines were isolated as byproducts in the preparation of ω-haloimines. The spectral data of diimines 3 are compiled in Tables 2 and 3. All diimines 3 are new compounds, and possess the E-configuration (due to the two methyl groups in the α-position) except for diimine 3d (R_1 = H, R_2 = Ph) where a mixture of E- and Z-isomers was obtained. Assigment of the E and Z configuration for product 3d was done by analogy with results obtained in the literature.[8-10] It is known that the *ortho* protons for imines obtained from aralkylketones have a value between 7.8-8.0 ppm (^{1}H-NMR spectrum) for the E-isomers and 6.9-7.1 ppm for the Z-isomers. The protons of the N-substituent (e.g. isopropyl) have also a higher δ-value (^{1}H-NMR) for the E-isomers than for the Z-isomers.[9,10] In analogy with these results, we conclude that the E/Z ratio for diimine 3d is 65/35. The diimines 3 can be readily hydrolyzed to the corresponding carbonyl compounds (see ref. 2 and 3 and Experimental Section). For example, the hydrolysis of 3d was performed under reflux with hydrochloric acid. After work-up, only 1,8-diphenyl-1,8-octanedione was obtained in 92 % yield, thus proving that the proposed structure of diimine 3d was correct.

The starting aldimines 1 (R_2 = H) were prepared by condensation of a primary amine and an aldehyde and the ketimines 1 (R_2 = H) were prepared by condensation of a carbonyl compound with a primary amine in the presence of titanium(IV) chloride.[11,12] In conclusion, the reaction of α-anions with dihaloalkanes leads to an efficient method for the preparation of diimines.

EXPERIMENTAL SECTION

All glassware was thoroughly dried in an oven (110°). The reactions were performed under a nitrogen atmosphere. THF was distilled from sodium benzophenone ketyl. Commercial reagents (diisopropylamine, n-BuLi, starting ketones, aldehydes, primary amines and dihaloalkanes) were used without further purification.

Synthesis of Diimines. General Procedure.- To a solution of lithium diisopropylamide (0.11 mol) at 0° in THF prepared from n-BuLi (0.11 mol) and diisopropylamine (0.20 mol) was added a solution of imine 1 (0.10 mol) over a period of 15 min. The deprotonation was complete after 2 hrs at 0° and then 0.05 mol dihaloalkane was added dropwise to the solution. After the addition, the reaction mixture was stirred overnight (∿ 14-15 hrs) while the temperature became ambient. The reaction mixture was then poured into water and extracted twice with pentane. The combined extracts were dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. After distillation the diimines were obtained in 62-95 % yield.

Synthesis of 1,8-Diphenyl-1,8-octanedione.- The distilled diimine 3d, prepared according to the procedure described above, was hydrolyzed with an aqueous HCl solution (10 equiv. of 2N HCl, reflux 1 day) to give, after extraction (CH_2Cl_2), drying ($MgSO_4$),evaporation of the solvent, 92 % yield of 1,8-diphenyl-1,8-octadione (4), mp. 92°, lit.[13] 85-87°, lit.[14] 86-87°, lit.[15] 91°. IR (KBr): 1685 cm^{-1}. (CO)

^1H-NMR($CDCl_3$): δ (ppm) 1.20-2.10 (8H,m,$CH_2-(\underline{CH_2})_4-CH_2$), 2.97 (4H,t,J=6.2Hz,2x$C\underline{H_2}$-C=O), 7.20-8.20 (10H,m,$C_6\underline{H_5}$).

^{13}C-NMR($CDCl_3$): δ (ppm) 200.2 (2x$\underline{C}$=O,s); 137.0 (2x$\underline{C}$q,s); 132.8, 128.5 and 128.0 (2x($\underline{C}$o, $\underline{C}$m and $\underline{C}$p), 3xd); 38.4 (t,2x$\underline{C}H_2$ C=O); 29.1 and 24.1 (2x$\underline{C}H_2$-$\underline{C}H_2$-CH_2-C=O,2xt).

Mass spectrum (70 eV) m/e (%): 294 (M^+;6); 176(4); 175(19);

174(3); 171(5); 157(4); 156(3); 133(4); 121(6); 120(37); 106 (10); 105(100); 91(4); 78(12); 77(40); 72(6); 71(4); 69 (4); 58(4); 57(5); 55(9); 51(10); 44(8); 43(14); 41(12); 40 (14).

TABLE 2. Spectral Data of Diimines 3

Cmpd	IR (C=N) cm^{-1}	^{1}H NMR ($CDCl_3$, δ)	Mass spectrum (m/e, %)
3a	1669	0.77(3H,d,J=6Hz,$C\underline{H}_3CH$); 0.89 and 0.94(12H,2xs,2x$(C\underline{H}_3)_2C$); 1.10(18H,s,2x$(C\underline{H}_3)_3C$); 0.80-1.50(5H,m,$C\underline{H}_2$-$C\underline{H}_2$-$C\underline{H}(C\underline{H}_3)$-);7.37 (2H,s,2x$C\underline{H}$=N)	no M^+; 293(3); 251(4); 250(21); 238(3); 210(3); 195(16); 172(4); 166(4); 154(6); 128(12); 127 (100); 126(12); 113(4); 112(37); 110(4); 109(4); 99(9); 98(6); 97(4); 96(6); 86(9); 84(10); 72(12); 71(24); 70(13); 69(9); 58(19); 57(67); 56(15); 55(16); 44(6); 43(13); 42(10); 41(19)
3b	1665	0.80(3H,d,J=6Hz,$C\underline{H}_3CH$); 0.93 and 0.98(12H,2xs,2x$(C\underline{H}_3)_2C$); 0.80-2.00(25H, m,$C\underline{H}_2$-$C\underline{H}_2$-$C\underline{H}C\underline{H}_3$ and 2x $C_6\underline{H}_{10}$); 2.60-3.20(2H,m, 2xC=N-C$\underline{H}$); 7.43(2H,s,2x C$\underline{H}$=N)	no M^+; 278(6); 277(26); 261(9); 208(8); 195(6); 180(6); 154(14); 153(100); 152(8); 112(25); 110 (23); 98(8); 84(8); 83(26); 82 (8); 81(6); 72(12); 71(6); 70 (9); 69(8); 67(8); 56(11); 55 (54); 44(9); 43(12); 42(6); 41 (25)
3c	1665	0.81(3H,d,J=6Hz,$C\underline{H}_3CH$); 0.94 and 0.99(12H,2xs, 2x$(C\underline{H}_3)_2C$); 1.11(12H, d,J=6Hz,2x$CH(C\underline{H}_3)_2$); 0.80-1.80(5H,m,$C\underline{H}_2$-$C\underline{H}_2$ -$C\underline{H}(CH_3)$); 3.23(2H,septet, J=6Hz,2x$C\underline{H}$-$(CH_3)_2$); 7.45 (2H,s,2xC$\underline{H}$=N)	no M^+; 238(6); 237(29); 196(7); 168(8); 140(6); 114(12); 113 (100); 112(7); 98(34); 85(8); 72(17); 70(17); 69(7); 55(13); 44(6); 43(32); 42(7); 41(11)

3d	1633	1.02 and 1.17(12H,2xd,J=6.2Hz, 2xCH(C$\underline{H}_3$)$_2$(E/Z)); 0.80-1.80(8H,m,CH$_2$-(C$\underline{H}_2$)$_4$-CH$_2$); 2.20-2.90(4H,m,2xC$\underline{H}_2$-C=N); 3.34 and 3.83(2H,2x septet,J=6.2Hz,2xC$\underline{H}$-(CH$_3$)$_2$ (E/Z)); 6.80-7.80(10H,m, 2xC$_6\underline{H}_5$)	376(M$^+$, 5); 333(12); 216(44); 214(10); 174(13); 172(10); 162(9); 161(56); 160(56); 146(23); 132(9); 105(30); 104(100); 91(10); 77(15); 58(10); 44(42); 43(25); 42(13)
3e	1665	1.01(12H,s,2x(C$\underline{H}_3$)$_2$C); 1.14(12H,d,J=6.4Hz,2x(C$\underline{H}_3$)$_2$CH); 1.00-1.50(8H,m,(C$\underline{H}_2$)$_4$); 3.27(2H, septet,J=6.4Hz,2xC$\underline{H}$(CH$_3$)$_2$); 7.50(2H,s, 2xC$\underline{H}$=N)	280(M$^+$, 1); 237(3); 236(19); 168(3); 166(3); 126(9); 114(10); 113(100); 112(6); 111(5); 99(3); 98(35); 84(6); 72(8); 71(3); 70(15); 69(6); 62(6); 60(6); 59(8); 44(7); 43(45); 42(6); 41(12)
3f	1669	1.00(12H,s,2x(C$\underline{H}_3$)$_2$CH); 1.12(18H,s,2x(C$\underline{H}_3$)$_3$C); 1.00-1.50(8H,m,(C$\underline{H}_2$)$_4$); 7.39(2H,s,2xC$\underline{H}$=N)	no M$^+$; 293(3); 251(7); 195(6); 140(8); 128(11); 127(100); 126(4); 125(4); 114(5); 113(3); 112(33); 102(3); 96(3); 95 (5); 86(3); 84(9); 72(5); 71(17); 70(9); 69(6); 58(8); 57(40); 56(9); 55(10); 44(4); 43(7); 42(4); 41(13)
3g	1671	0.99(12H,s,2x(C$\underline{H}_3$)$_2$C); 1.15(18H,s,2x(C$\underline{H}_3$)$_3$C); 1.00-1.50(6H,m,(C$\underline{H}_2$)$_3$); 7.40(2H,s,2xC$\underline{H}$=N)	no M$^+$; 171(14); 157(13); 156(100) 154(7); 138(10); 115(10); 100(8); 99(55); 98(19); 86(7); 82(20); 70(23); 69(8); 59(71); 58(19); 57(32); 56(12); 55(19); 46(6); 43(74); 42(20); 41(50)

TABLE 3. ^{13}C-NMR Data of Diimines 3 (δ in $CDCl_3$)

	$\underline{C}$=N	C=N-$\underline{C}$	$\underline{C}$-C=N	$C(\underline{C}H_3)_2$ (q)	$CH(\underline{C}H_3)$ (q)	CH_2(t) and $\underline{C}H(CH_3)$ (d)	Other signals
3a	165.3(d) 164.6(s)	56.1(s) 56.0(s)	41.8(s) 38.6(s)	24.9; 24.8; 22.4; 21.4	14.1(q(br))	41.2; 39.6 and 26.3 (2xt(br), 21xd(br))	29.8(($\underline{C}H_3)_3C$,q)
3b	169.5(d) 168.9(d)	70.0(d) 69.8(d)	41.9(s) 38.6(s)	25.2; 24.8; 22.7; 21.3	14.0(q(br))	41.0; 39.5 and 26.3 (2xt(br), 1xd(br))	34.4; 25.7 and 24.9(3xt,$\underline{c}$-Hex)
3c	169.1(d) 168.5(d)	61.7(d) 61.5(d)	41.8(s) 38.6(s)	25.0[a]; 24.8[a]; 22.5; 21.4	14.1(q(br))	41.0; 39.5 and 26.2 (2xt(br), 1xd(br)	24.9[a](($\underline{C}H_3)_2CH$;q)
3d[b]	169.3; 169.1; 166.2; 166.0; 140.9; 140.8; 139.0; 129.0; 128.9; 128.5; 128.3; 128.2; 128.0; 127.7; 127.6; 127.0; 126.1; 51.9; 50.7; 42.3; 42.2; 29.5; 29.4; 29.1; 28.9; 28.6; 28.5; 27.5; 27.5; 26.4; 26.2; 24.2; 24.1; 23.9						
3e	168.4(d)	61.5(d)	38.4(s)	24.9[a]	-	40.6(t); 25.0(t)	24.2[a](($\underline{C}H_3)_2CH$;q)
3f	164.8(d)	56.0(s)	38.4(s)	24.8	-	40.7(t) 25.1(t)	29.8(($\underline{C}H_3)_3C$;q)
3g	164.9(d)	56.1(s)	38.6(s)	24.9	-	41.5(t) 19.2(t)	29.8(($\underline{C}H_3)_3C$;q)

a) or vice versa

b) due to the presence of several isomers (E/E, Z/E and Z/Z), it was not possible to attribute the ppm values to the different carbon atoms (it is possible that some values are overlapping).

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