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A GENERAL AND CONVENIENT ROUTE TO α-DIKETANILS AND α-DIKETONES[1]

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Several methods[2], including one recently reported[3] by us, are available for the synthesis of ketimines. However, we are not aware of any general route to α-diketimines[4]. We now report a convneient and a fairly general cyanide-ion catalyzed transformation of aromatic aldimines 1 to α-diketanils 12 in good to excellent yields (Table 1). We also find that dianils 12 on treatment with acid can be efficiently converted to α-diketones 13 (Scheme 1).

Treatment of a 0.66M solution of imine 1 in dry dimethyl sulfoxide (DMSO) with an equivalent amount of sodium cyanide at 20° for a period of 72 hours afforded α-diketanils 12. A small amount of anilide 10 was also obtained in some cases. The product ratios were sensitive to both concentration of azomethine 1 and to temperature. Thus, a 0.13M solution of 1a gave only dianil 12a (89%) at 20°; when the temperature was raised to 59-60° a 0.66M solution gave 12a (41%) and benzanilide (48%). The identity of the α-diimines 12 was established by their infrared spectra (strong absorption near 1610 cm^{-1}), elemental analysis and in the case of dianil 12a, by comparison with an authentic sample[4]. Furthermore, the diketimines 12 on shaking with hydrochloric acid were easily converted to the known α-diketones 13 in almost quantitative yield.

The conversion of 1a to 12a proceeds to completion with as little as 0.1 mole equivalent of cyanide ion demonstrating that cyanide ion acts as a catalyst[5]. That the cyanide ion is

TABLE 1

Syntheses of α-Diketanils and α-Diketones

	Ar	Ar$_1$	Diketanil 12		Anilide 10		Diketone 13
			Mp, °C	Yield %	Mp, °C	Yield % (Approx.)	Mp, °C
a	phenyl	phenyl	144-5[a]	77	160-1[b]	3-5	94-5[f]
b	p-chlorophenyl	phenyl	155-6	64	195-6[c]	7	198-200[g]
c	o-chlorophenyl	phenyl	216-7	83	—	—	133-4[h]
d	p-tolyl	phenyl	147-8	72	—	—[d]	104-5[i]
e	p-anisyl	phenyl	150-1	62	170-1[e]	2-3	131-3[j]

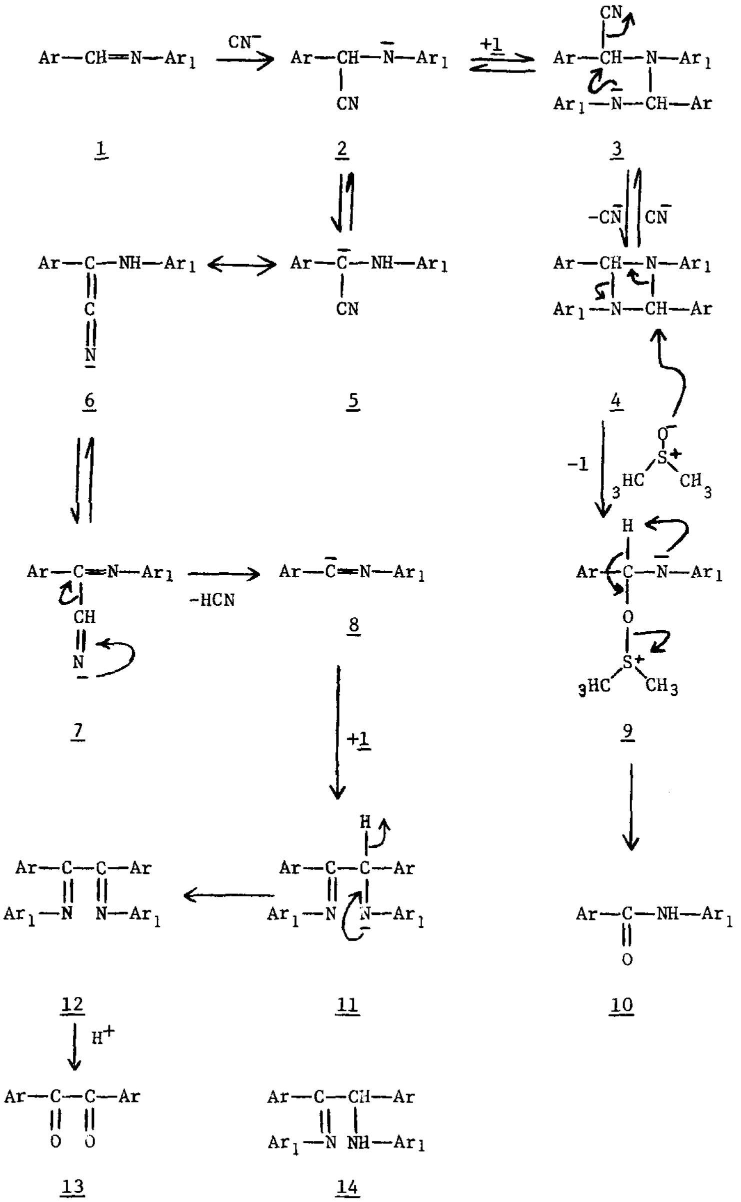
[a] Lit.[4a] mp 144°. [b] Lit. mp 160°: M. Siegfried, Chem. Ber., 25, 2601 (1892). [c] Lit. mp 194-6°: A. Hantzsch, Chem. Ber., 24, 506 (1891). [d] Anilide, perhaps, present in small quantities could not be isolated. [e] Lit. mp 168-9°: R. Haller, Compt. Rend., 121, 190 (1895). [f] Lit. mp 94-5°: I. A. Pearl and W. M. Dehn, J. Am. Chem. Soc., 60, 57 (1938). [g] Lit. mp 200°: A. Hantzsch and W. H. Glower, Chem. Ber., 40, 1519 (1907). [h] Lit. mp 133°: C. V. Deliwala and S. Rajgopalan, Proc. Indian Acad. Sci., 31A, 107 (1950); Chem. Abstr., 45, 6178 (1951). [i] Lit. mp 104-5°: D. Vorlander, Chem. Ber., 46, 2455 (1911). [j] Lit. mp 131-3°, Ref. as in h.

specific for this reaction was shown by the observation that azomethine 1a either alone or in the presence of sodium hydroxide under similar conditions did not yield any dianil 12a or anilide 10a, only starting material being recovered quantitatively[6].

Aldimines derived from benzaldehyde and other aromatic amines (besides aniline) such as p-chloroaniline, p-toluidine and p-anisidine smoothly undergo this reaction to afford the corresponding dianils in 73, 85 and 75% yields respectively. The reaction, however, fails with benzlidenecyclohexylamine, p-hydroxybenzylideneaniline and p-dimethylaminobenzlideneaniline.

The mechanism of this novel reaction would appear to resemble that of the benzoin condensation , where the intermediate 14 (a formal benzoin type condensation product from 1) could undergo oxidation to 12 by the solvent DMSO . This attractive possibility seems unlikely since the reaction 1a to 12a proceeds in over 80% yield even in a poorly oxidizing solvent dimethyl-

SCHEME 1



formamide (DMF). Furthermore, Becker[9] has recently shown that 14 when $Ar=Ar_1=C_6H_5$ is unchanged in basic DMSO solution. The mechanism outlined in Scheme 1 is tendered for this reaction. Addition of cyanide ion to azomethine 1 affords N-anion 2 which rearranges to carbanion 5 by a prototropic shift. Carbanion 5 via its canonical structure 6 is readily transformed to tautomer 7 which undergoes fragmentation to azomethinyl carbanion 8 and hydrogen cyanide. Nucleophilic addition of carbanion 8 to imine 1 provides intermediate N-anion 11, loss of hydride ion from which delivers dianil 12[10]. The hydride ion[11] presumably removes a proton from hydrogen cyanide to regenerate cyanide ion, the catalytic role for which is therefore obvious. The formation of anilide 10 possibly results from the addition of anion 2 to 1 to afford intermediate 4 via anion 3. Nucleophilic attack by DMSO on 4 gives zwitterion 9 which collapses to 10. In feebly oxidizing DMF the intermediate 4 returns to N-anion 2 either directly or through anion 3 and thence yields the dianil 12.

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3. J. S. Walia, L. Heindl, H. Lader and P. S. Walia, Chem. and Ind., (London) 155 (1968).
4. Isolated examples of a few α-diketimines are known. For example, (a) benzildianil has been obtained in 16% yield by heating aniline and benzil in the presence of P_2O_5at 200°, M. Siegfried, Chem. Ber., 25, 2601 (1892); G. Reddelien, Chem. Ber., 46, 2723 (1913). (b) For similar syntheses of diacetyldianil, diacetyl-bis- (cyclopropylimid) and diacetyl-bis- (benzylimid), see H. Bock and H. tom Dieck, Chem. Ber., 100, 228 (1967).
5. The reaction is reminiscent of the benzoin condensation. See W. S. Ide and J. S. Buck in Organic Reactions, Vol. IV, R. Adams, Ed., John Wiley & Sons, Inc. New York, 1948, p 269.
6. The possibility of the reaction proceeding via prior hydrolytic cleavage of 1 to an aldehyde and aniline was dismissed since the reaction of benzaldehyde, aniline and cyanide ion in DMSO gave only benzoin.
7. E. S. Gould, "Mechanism and Structure in Organic Chemistry", Henry Holt & Co., 1959, p 394.
8. For the role of DMSO as an oxidizing agent, see N. Kharasch and B. S. Thyagarajan, Quat. Rep. Sulfur, 1, 1 (1966).
9. H. Becker, J. Org. Chem., 29, 2891 (1964).
10. The reaction is evidently a case of oxidative coupling involving azomethinyl carbanion. For some examples of oxidative dimerization proceeding via carbanions, see (a) C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor and A. E. Bradhag, J. Am. Chem. Soc., 78, 1653 (1956). (b) C. G. Swain and E. R. Thornton, J. Am. Chem. Soc., 83, 4033 (1961).
11. The solvent DMSO or DMF could also partly trap the hydride ion.