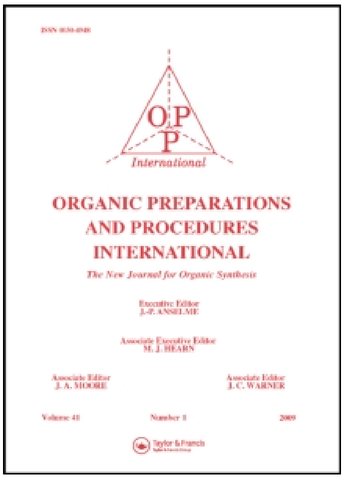

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REACTION OF ENAMINES OF SOME BICYCLIC AND MONOCYCLIC KETONES WITH 2,4-DINITROCHLOROBENZENE AND 2-CHLORO-3,5-DINITROTHIOPHENE[1]

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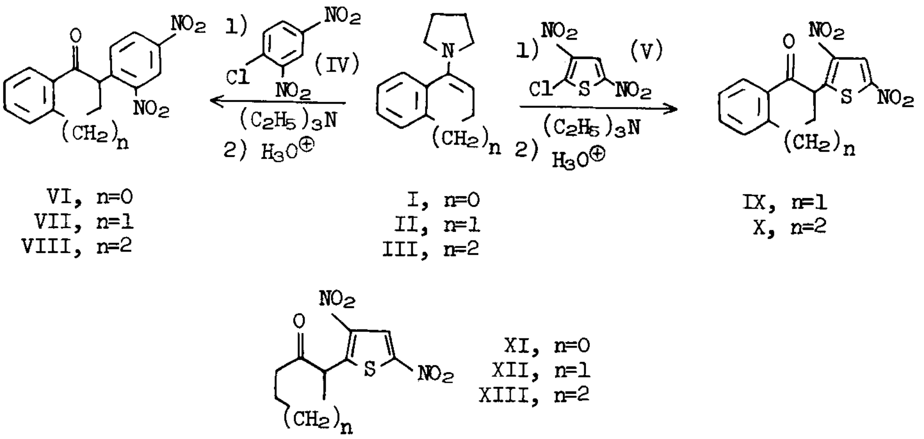
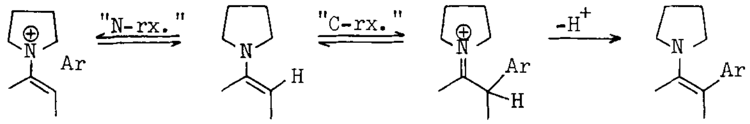


The reaction of pyrrolidine enamines of monocyclic ketones with nucleophilic-labile aromatics, such as 2,4-dinitrochlorobenzene (IV) and certain chloronitropyridines, has been described.[2] Earlier it was reported that α-methylation of II proceeded in low yield compared to III because of steric factors; due to reaction at nitrogen being reversible, α-3-oxobutylation of II was improved though still less than for III.[1] Briefly probing further, we treated I-III with IV under conditions similar to those of Kuehne[2a] (an extra acid treatment during hydrolysis was added) and obtained moderate yields of VI-VIII. This reaction was extended to a heteroaromatic halide not previously reacted with enamines, 2-chloro-3,5-dinitrothiophene (V), to yield IX and X from II and III in high yields. Pyrrolidine enamines of some monocyclic ketones were also reacted with V to give XI-XIII in low yields due to the less-than-optimal conditions used.

It is not surprising that yields of the α-arylated ketones (VII, IX) from II were much improved over that of α-methylation.[1] The nature of the arylation intermediate formed between IV or V and triethylamine, reversible "N-reaction" as well as "C-reaction" (including loss of displaced substituent) involving tetrahedral carbon intermediates,[3] and/or the ease of α-proton loss[2] may play roles in determining yields and may well overcome possible steric factors.



Ar = 2,4-Dinitrophenyl, 3,5-Dinitrothienyl

EXPERIMENTAL[4]

3-N-Pyrrolidino-1-indene (I). Pyrrolidine (0.80 mole), 1-indanone (0.19 mole) and p-toluenesulfonic acid (0.5 g) were refluxed in benzene (130 ml) for one day,[5] subsequent distillation yielding 65% of I, bp 115-119° (0.2 mm), lit.[6] 142-144° (2.0 mm), n_D^{23} 1.6012; ν_{max}^{neat} 3019-3080 (3 peaks), 1593, 1570, 1558 (sh) cm^{-1}; nmr (CCl_4) δ 4.93 (t, *J* 2.6 Hz, vinyl H); $\lambda_{max}^{cyclohexane}$ 222 (ε 10,900), 283 mμ (4,700).

Anal. Calcd for $C_{13}H_{15}N$: C, 84.27; H, 8.16. Found: C, 83.98; H, 8.24.

General procedure for VI-X. The procedure outlined by Kuehne[2a] was adapted, 0.020-0.033 mole of 2,4-dinitrochlorobenzene or 2-chloro-3,5-dinitrothiophene[7] being stirred under nitrogen with an equivalent of triethylamine in methylene chloride to which an equivalent of the requisite enamine (I, II[1] or III[1]) was added at 0°. After one day (25°) and subsequent solvent

TABLE

The α-2,4-Dinitrophenyl- and α-3,5-Dinitro-2-thienyl Ketones

Compd	Yield, %	Mp, °C	$\nu^{C=O}_{max}$ [a] cm^{-1}(KBr)	nmr, ppm($CDCl_3$) [b] $-\overset{O}{\overset{\|}{C}}-C\underline{H}$	Formula	Analysis, % Calcd C	Calcd H	Found C	Found H
				α-2,4-Dinitrophenyl-					
VI	26	143.5-144.5	1696-1706 (d)	4.47 (q)	$C_{15}H_{10}N_2O_5$	60.40	3.38	60.21	3.69
VII	55	157-159	1681	4.64 (q)	$C_{16}H_{12}N_2O_5$	61.53	3.88	61.80	3.99
VIII	30	104-105.5	1689	4.74 (t?)	$C_{17}H_{14}N_2O_5$	62.57	4.32	62.71	4.61
2-(2,4-Dinitrophenyl)-1-cyclohexanone (XV) [c]		97-99 (lit.[2] 99-100)	1705	4.47 (q)					
semicarbazone [c]		118-120	-	-	$C_{13}H_{15}N_5O_5$	48.59	4.71	48.63	4.77
				α-3,5-Dinitro-2-thienyl-					
IX	79	174.0-175.5	1678	5.1 (m)	$C_{14}H_{10}N_2O_5S$	52.82	3.17	53.15	3.23
X	69	170-172 [d]	1675	5.5 (m)	$C_{15}H_{12}N_2O_5S$	54.21	3.63	54.46	3.67
XI	19	114.5-116.5 [e]	1748	4.48 (q)	$C_9H_8N_2O_5S$	42.18	3.15	41.89	3.29
XII	27	142-144	1706	4.96 (q)	$C_{10}H_{10}N_2O_5S$	44.44	3.73	44.35	3.98
XIII	14	105-107	1706	5.20 (q?)	$C_{11}H_{12}N_2O_5S$	46.47	4.26	46.67	4.50

[a] VI-VIII and XV: $\nu^{NO_2}_{max}$ 1523-1536 and 1342-1350 cm^{-1}; IX-XIII: $\nu^{NO_2}_{max}$ 1546-1558, 1505-1520 and 1330-1346 cm^{-1}.

[b] VI-VIII and XV: δ 8.70-8.82 (d, 1H, J^{meta} 2.2 ± 0.2 Hz, proton ortho to both NO_2); IX-XIII: δ 8.30-8.39 (s, 1H, thiophene H).

[c] Prepared by E. Wahrenbrock (Spring, 1958). [d] Chloroform-methanol. [e] Ether-methanol, a drop dilute hydrochloric acid added.

evaporation, the residue was stirred with 100 ml of 1 N (VI-VIII) or 3 N (IX, X) hydrochloric acid. After 12-24 hours (25°) the acid phase was decanted and the acid treatment of the residue was repeated. On standing (0°) the acid portions deposited crystals; for VI-VIII, the acid portions were heated on a steam bath for two-five hours prior to cooling. Recrystallization was from methanol except as noted. See Table for details.

2-(3,5-Dinitro-2-thienyl)-cyclanones (XI-XIII). The procedure for VI-X was followed except that either V was added to a mixture of triethylamine and the appropriate pyrrolidine enamine[5] of the ketone (for XI, XIII) or the enamine was added to V followed by rapid addition of triethylamine (for XII). Large quantities of black residue (insoluble in acid, base) accompanied the preparations of XI and XII. The crude product of XII was contaminated by XIV, manually separated and established by mixed mp with authentic material (see below).

2-(N-pyrrolidino)-3,5-dinitrothiophene (XIV). Brief heating of 0.013 mole V in methanol with excess pyrrolidine gave a 69% yield of XIV, mp 122-4° (methanol); ν_{max}^{KBr} 1565, 1533 and 1325 cm^{-1} (nitro); $\lambda_{max}^{CH_3OH}$ 243 (ε 10,500), 370 (13,500) and 418 mμ (15,900); nmr ($CDCl_3$) δ 8.23 (s, 1 H, thiophene H).

Anal. Calcd. for $C_8H_9N_3O_4S$: C, 39.50; H, 3.73. Found: C, 39.68; H, 3.92.

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