Organometallic Route to *N*-Substituted 1*H*-1,2-Diazepines[1]

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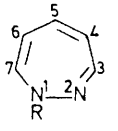
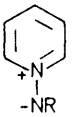
Summary 1*H*-1,2-Diazepineirontricarbonyl complexes (**3b**—**k**) have been synthesized from (**3a**); some of these have been decomplexed to 1*H*-1,2-diazepines (**1b**—**f**, **1h**) thus providing a new route to this class of heterocycles.

1*H*-1,2-DIAZEPINES (**1**, R = COR, CO_2R, SO_2R) represent a recently discovered class of heterocyclic compounds whose preparative availability is dependent on the photolysis of the corresponding *N*-iminopyridinium ylides (**2**).[2]† The utility of this method for the synthesis of diversely *N*-substituted 1*H*-1,2-diazepines has been significantly limited by competing and exclusive photochemical N–N fragmentation of the ylides, *e.g.*, (**2**), R = COMe,[3] CSNHR,[4] CN,[2b] Ph[5] and by the inadequate scope of the available routes[2] to ylides, *e.g.*, (**2**), R = $COCH_2Cl$, $COCF_3$, CH_2COPh[6] and their precursor *N*-aminopyridinium salts.[2b] We report on a new general synthesis of 1*H*-1,2-diazepine irontricarbonyl complexes (**3c**—**k**) and the decomplexation of (**3b**—**f**, **3h**) into compounds (**1b**—**f**, **1h**). We thereby provide a new entry to *N*-substituted 1*H*-1,2-diazepines which circumvents some of the above limitations and which, in its conceptual approach, may have practical consquences in other areas of heterocyclic synthesis.

The approach is based on using the ylide (**2b**) as the single source of the 1*H*-1,2-diazepine ring system and takes advantage of earlier observations regarding the behaviour



(1)



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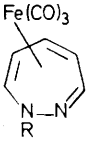

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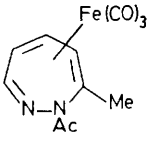

(4)

a; R = H
b; R = COMe
c; R = COPh
d; R = COCH=CHPh
e; R = $COCH_2Cl$
f; R = $CO_2CH_2CCl_3$
g; R = Me
h; R = CH_2Ph
i; R = $CH_2CH{=}CH_2$
j; R = $COCF_3$
k; R = CN

† An alternative method from pyrylium and thiapyrylium salts is restricted to the synthesis of 3,5,7-triaryl-1,2(1*H*)-diazepines (D. J. Harris, G. Y.-P. Kan, V. Snieckus, and O. Buchardt, *Synthesis*, 1975, **603** and refs. therein) and appears to hold little promise for the direct preparation of less substituted derivatives (H. C. van der Plas, 'Ring Transformations of Heterocycles,' Academic Press, New York, 1973, Vol. 2, pp. 4, 28; G. Y.-P. Kan, unpublished results).

of the fluxional tricarbonyl(4—7-η-1*H*-1,2-diazepine)iron(0) (**3a**)[7] and the decomplexation of diene-irontricarbonyl adducts.[8] Complex (**3a**), obtained in quantitative yield from (**3b**)[7b] was allowed to react with acyl chlorides and alkyl bromides or iodides to give the *N*-substituted derivatives (**3c—i**) (Table). The yield of the *N*-methyl complex (**3g**) was considerably improved by using an alternative set of conditions‡ given in the Table. Furthermore, treatment of (**3a**) with $(CF_3CO)_2O$ and BrCN under otherwise similar conditions provided the interesting derivatives (**3j**) and (**3k**), respectively.

TABLE. Synthesis and decomplexation of *N*-substituted tricarbonyl(4—7-η-1*H*-1,2-diazepine)iron(0) derivatives[a]

Acylation–alkylation[b] Compound	Yield,[d] %	Decomplexation[c] Compound	Yield,[d] %
(**3b**)	>95	(**1b**)	91
(**3c**)	86	(**1c**)	78
(**3d**)	>95	(**1d**)	94
(**3e**)	>95	(**1e**)	41
(**3f**)	>95	(**1f**)	86
(**3g**)	30 (70)[e]		
(**3h**)	89	(**1h**)	30
(**3i**)	75		
(**3j**)	94		
(**3k**)	82		

[a] With the exception of (**1b**), (**1c**), (**3b**), (**3c**), and (**3h**), (refs. 2b and 7), all the compounds are new and have been characterized by analytical, and i.r., n.m.r., and mass spectral data in comparison with known derivatives (ref. 7b). [b] Acylation: 1 equiv. RCOCl, $NaHCO_3$, anhydrous PhH, room temp., 1—2 h. Alkylation: excess RX, $NaHCO_3$, room temp., 20 h. [c] At least 20-fold molar excess of *freshly sublimed* $Me_3N{\rightarrow}O$, anhydrous PhH, room temp., N_2, 3 h. $Me_3N{\rightarrow}O{\cdot}2H_2O$ gives unsatisfactory results (compare ref. 8). [d] After chromatography on silica gel. [e] $MeOSO_2F$, $EtN(Pr^i)_2$, CH_2Cl_2, 0 °C to room temp.

Based on our protonation studies of (**3a**)[7b] it may be expected that electrophilic reaction by acylating and alkylating agents would proceed by attack at N-2 followed by N-1 deprotonation and diene–$Fe(CO)_3$ reorganization. However, acetylation (Ac_2O, room temp., 30 min) of the non-fluxional 3-methyl derivative of (**3a**) afforded only the 3-methyl derivative of (**3b**) and not its isomer (**4**) thus indicating preference for N-1 acylation perhaps as a consequence of a steric effect.

Decomplexation of compounds (**3b—f, 3h**) by adaptation of Shvo's procedure[8] gave the 1*H*-1,2-diazepines (**1b—f, 1h**) (Table). Other reagents reported to be moderately successful in releasing non-nitrogen containing organic ligands from their diene–$Fe(CO)_3$ complexes[9] led uniformly to extensive decomposition. Finally, decomplexation of (**3h**) afforded the unstable (**1h**) which is the first representative of a simple *N*-alkyl-1*H*-1,2-diazepine and is indicative of the directions of our further efforts.

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‡ This experiment was first performed by J. A. Oakleaf in these laboratories.

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