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The Synthesis and Properties of Three Isomers of 1-Troponyl-1H-1,2-diazepine

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The substitution reaction of 2-halotropones or 2-tosyloxytropone with tricarbonyl(4-7-η-1H-1,2-diazepine)iron afforded three isomers of tricarbonyl(4-7-η-1-troponyl-1H-1,2-diazepine)iron in good combined yield: three complexes were decomplexed to novel three isomers of 1-troponyl-1H-1,2-diazepine.

Although substituted 1H-1,2-diazepines have been synthesized photochemically from 1-iminopyridinium ylides,[1] the utility of this method for the preparation of 1-substituted 1H-1,2-diazepines has been limited by the existence of competing or exclusive N-N bond cleavage of the ylides.[2,3] The alkylation or acylation of tricarbonyl(4-7-η-1H-1,2-diazepine)iron[4] and subsequent decomplexation provide a new method of circumventing the above limitation.[5] Although no 1-vinyl-[6] or 1-aryl-1H-1,2-diazepine[3] has been prepared so far, these compounds are interesting because of their stabilities and properties. Thus, we have previously studied the nucleophilic addition of tricarbonyl(4-7-η-1H-1,2-diazepine)iron with activated acetylenes to provide the first example of 1-vinyl-1H-1,2-diazepine derivatives.[7] In connection with this study, we now report the first synthesis of three isomers of 1-troponyl-1H-1,2-diazepine by the substitution reaction of 2-halotropones (1a-c) or 2-tosyloxytropone (1d) with tricarbonyl(4-7-η-1H-1,2-diazepine)iron (2) followed by decomplexation reaction.

A typical procedure of the substitution reaction involves heating of tropones 1a-d (1 mmol) with 2 (1 mmol) in anhydrous benzene (10 cm^3) in the presence of diazabicycloundecene (DBU) (1.2 mmol) under reflux. The separation of the products through TLC on silica gel (hexane-AcOEt-5/1) afforded tricarbonyl(4-7-η-1-troponyl-1H-1,2-diazepine)irons (3-5) in good combined yields as indicated in Table 1. The products 3-5 are fairly stable and they can be stored at room temperature for more than six months. The structures of new compounds 3-5 were elucidated from their analytical and physical data[8] [e.g. 3: mp 133-135 °C; IR ($CHCl_3$), 2050, 1977, 1622, 1565 cm^{-1}; 4: mp 177-178 °C; IR ($CHCl_3$), 2054, 1981, 1637, 1560 cm^{-1}; 5: mp 163-164 °C; IR ($CHCl_3$), 2054, 1982, 1630, 1565, 1510 cm^{-1}].

Based on the reaction of 2 with electrophile[5] and our previous study,[7] it may be expected that the present reaction of 2 proceeds by attack of N2 onto 1a-d followed by proton migration to give enol and concomitant diene-$Fe(CO)_3$ reorganization. Then, the enol-keto tautomerization followed by HX elimination

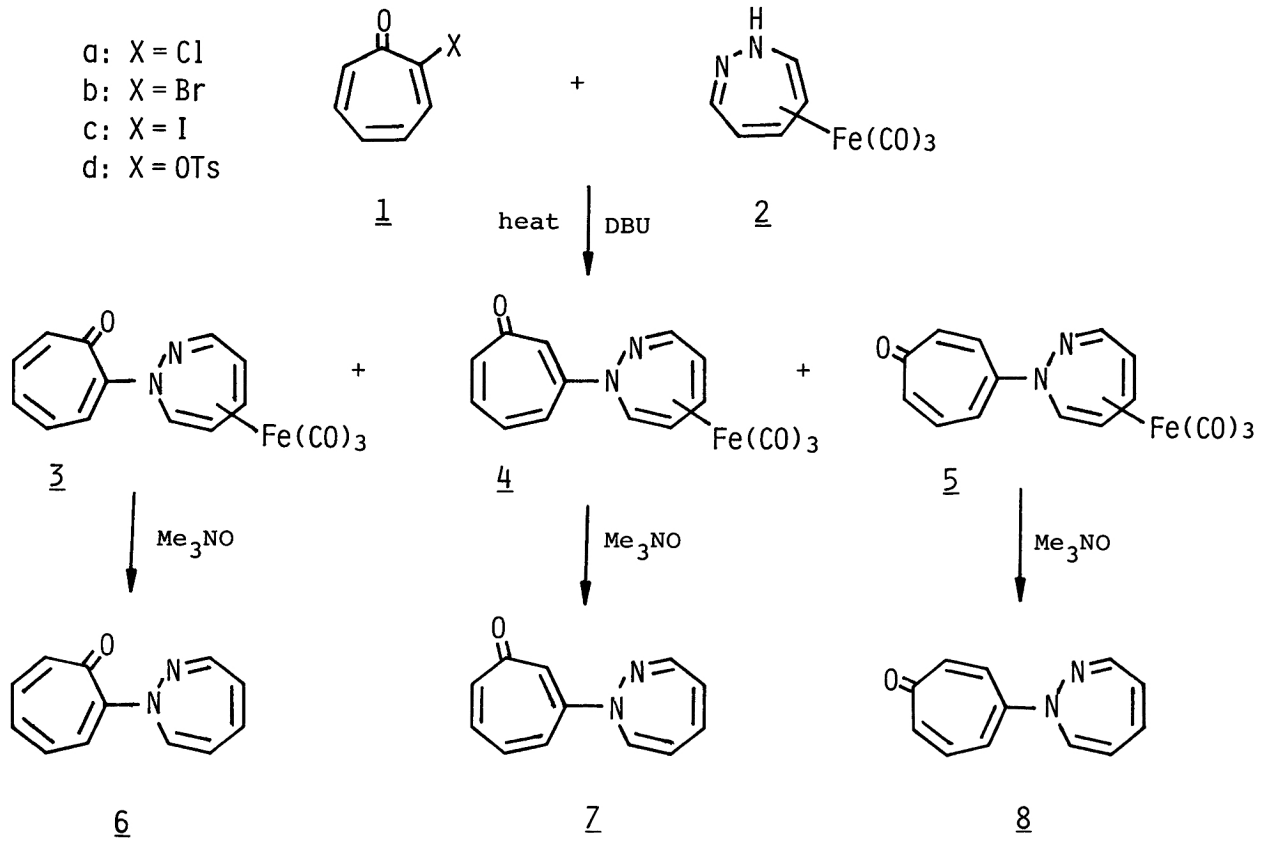


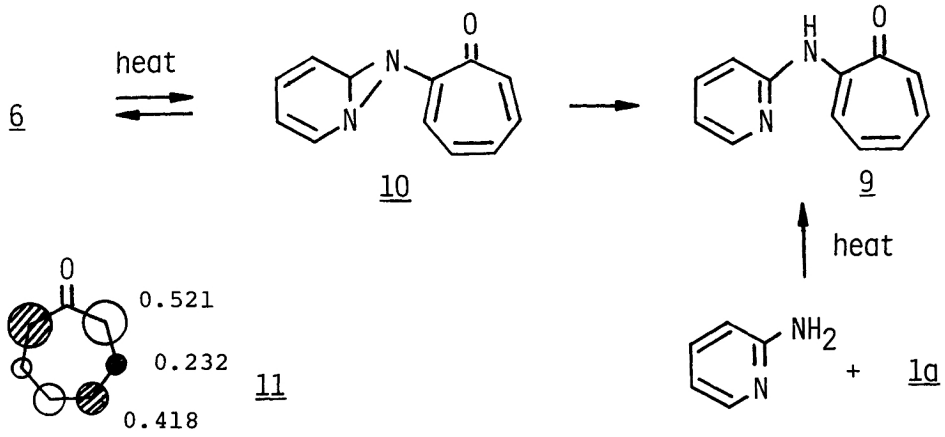
Table 1. Results for the reaction of 1a-d with 2 [a]

	Product Yield/%			Recovery/%	
Compd.	3	4	5	1	2
1a	80	6	4	7	5
1b	68	13	9	3	5
1c	70	12	7	7	4
1d	82	1	2	11	5

a) Reactions were carried out in benzene solution under reflux for 1 h.

results in the formation of 3-5. The nucleophilic substitution onto tropones carrying a mobile substituent at C2 have been known to take place either on C2 (normal substitution) or C7 (abnormal substitution) to give 2-substituted tropones.[9] It is not concluded a priori whether normal or abnormal substitution is operative in the formation of 3-5. The formation of 3- and 4-substituted tropones such as 4 and 5 is anomalous in the reaction of 1a-d with amines,[9] although strong nucleophile, such as OH^-, has been known to attack on C1, C2, C3, C4, or C5, and C6 of tropone nucleus to give benzenoid products.[10] The products 4 and 5 seem to arise from addition of 2 on C3 and on C5 of 1, respectively.

Decomplexation[11] of 3 (1 mmol) with dehydrated trimethylamine oxide (8 mmol) in anhydrous acetone at room temperature for 4h followed by flash column on alumina (using ether as the eluant) afforded 6 in a 76% yield. The compounds 4 and 5 were decomplexed similarly to give 7 and 8 in 76 and 44% yields, respectively.



The structures of new compounds 6-8 were assigned on the basis of the spectral data.[8,12]

The compound 6, the diazepine moiety of which is fully conjugated with the tropone nucleus, is very unstable in neat or even in chloroform solution, and it decomposes completely at room temperature to give an intractable tar after 2 days. However, heating of 6 in benzene under reflux for 30 min afforded tarry materials and 9 [mp 97-98 °C; 16% yield], which was characterized by the independent synthesis using 1a and 2-aminopyridine. The facile isomerization of 6 to 9 seems to proceed via 10.[1] The equilibrium between 6 and 10 is considered to lie on the side of 6. However, the LUMO[13] of tropone (depicted in 11) accepts the lone pair electrons on the nitrogen atom of 6 so as to shift the equilibrium of 6⇌10 to the side of 10. This electronic interaction also causes to weaken the N-N bond of 10.[14] Thus, the facile N-N bond cleavage of 10 results in the formation of 9 irreversibly. The degree of this type of electronic interaction is dependent on the coefficient of LUMO (tropone). Therefore, one may compare this type of electronic interaction of 6, 8, and 7, which is expected to be decreased in that order, with their stabilities.

The absorption band at the longest wavelength region in the UV spectra[12] of 6, 8, and 7, is shifted to the shorter wavelength in that order. The compound 8, the diazepine moiety of which is located at C4 of the tropone nucleus, is unstable but it can be stored for 2 days in chloroform solution without any decomposition. In contrast, the compound 7, the diazepine moiety of which is located at C3 of the tropone nucleus, is stable for 1 month in chloroform solution without appreciable decomposition. However, heating both of 7 and 8 in benzene under reflux for 24 and for 6 h, respectively, afforded intractable oily materials.

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12) For 6: red oil; ^{1}H NMR ($CDCl_3$), δ=5.86 (1H, ddd, J=7.0, 5.4, 1.0 Hz), 6.33 (1H, broad d, J=7.0 Hz), 6.37 (1H, ddt, J=11.0, 3.4, 1.0 Hz), 6.6-6.9 (2H, m), 6.9-7.3 (3H, m), 7.55 (1H, dd, J=3.4, 0.8 Hz), 7.56 (1H, dd, J=10.1, 0.9 Hz); ^{13}C NMR ($CDCl_3$), δ=181.4 (s), 157.7 (d), 153.5 (s), 140.3 (d), 139.6 (d), 136.8 (d), 136.4 (d), 134.7 (d), 129.2 (d), 127.4 (d), 117.3 (d), 116.5 (d); IR ($CHCl_3$), 1619, 1581, 1558 cm^{-1}; λ_{max} (EtOH) (logε), 274 (3.95), 354 (3.94), 412 (3.95). For 7: yellow oil; ^{1}H NMR ($CDCl_3$), δ=5.9-6.2 (2H, m), 6.43 (1H, ddt, J=10.8, 3.2, 1.0 Hz), 6.70 (1H, dddd, J=10.8, 3.7, 1.5, 1.0 Hz), 6.8-7.1 (4H, m), 7.2-7.5 (1H, m), 7.55 (1H, dd, J=3.2, 1.0 Hz); ^{13}C NMR ($CDCl_3$), δ=184.4 (s), 158.3 (d), 151.6 (s), 142.2 (d), 138.4 (d), 133.5 (d), 132.2 (2C, d), 130.5 (d), 127.2 (d), 121.5 (d), 117.0 (d); IR ($CHCl_3$), 1644, 1615, 1587 cm^{-1}; λ_{max} (EtOH) (logε), 303 (4.18), 333 (sh, 3.98). For 8: red oil; ^{1}H NMR ($CDCl_3$), δ=5.9-6.2 (2H, m), 6.42 (1H, ddt, J=11.0, 3.3, 1.1 Hz), 6.70 (1H, dddd, J=11.0, 3.7, 1.8, 1.1 Hz), 6.8-6.9 (2H, m), 7.0-7.2 (2H, m), 7.47 (1H, dd, J=13.0, 2.4 Hz), 7.53 (1H, dd, J=3.3, 1.1 Hz); ^{13}C NMR ($CDCl_3$), δ = 186.2 (s), 158.5 (d), 151.8 (s), 141.7 (d), 138.8 (d), 137.4 (d), 134.1 (d), 132.0 (d), 130.9 (d), 128.5 (d), 121.9 (d), 110.7 (d); IR ($CHCl_3$), 1635, 1614, 1591, 1555 cm^{-1}; λ_{max} (EtOH) (logε) 296 (3.63), 374 (4.16).
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