Cycloadditions of Diphenylnitrilimine with Tropone and with Tricarbonyltroponeiron. Thermal [1,5] Sigmatropic Rearrangements of the [$_{\pi}6_s$ + $_{\pi}4_s$] Cycloadducts of 1,3-Dipoles with Tropone

Milena Bonadeo, Carlo De Micheli, and **Remo Gandolfi,*** Istituto di Chimica Organica dell'Università, Via Taramelli 10, 27100 Pavia, Italy

The reaction of diphenylnitrilimine (benzonitrile *N*-phenylimide) with tropone has been reinvestigated and eight products have been detected. In addition to the [$_{\pi}6_s$ + $_{\pi}4_s$] cycloadduct formed by reaction at positions 2 and 7 of tropone, both the regioisomeric [$_{\pi}2_s$ + $_{\pi}4_s$] adducts involving positions 2 and 3 and positions 4 and 5 were obtained. The reaction of tricarbonyltroponeiron, which was more reactive than tropone itself, gave a mixture of two regioisomers. The specific [1,5] sigmatropic rearrangement of the [6 + 4] cycloadducts of diphenylnitrilimine and benzonitrile oxide with tropone, which involves selectively the sp^2 carbon atom instead of either the oxygen or the nitrogen atom of the 1,3-dipole have been also studied.

HOUK and his co-workers reported the reaction of diphenylnitrilimine (benzonitrile *N*-phenylimide) (1a) with tropone (2) to give a mixture of the [$_{\pi}6_s$ + $_{\pi}4_s$] (3a) and [$_{\pi}2_s$ + $_{\pi}4_s$] cycloadducts in 5 and 29% yield, respectively.[1] The [$_{\pi}2_s$ + $_{\pi}4_s$] cycloadduct was tentatively assigned structure (4a) on the basis of the result of the reaction of the same 1,3-dipole (1a) with methyl crotonate, which gave methyl 4-methyl-1,3-diphenyl-Δ^2-pyrazoline-5-carboxylate (dominant product) and its regioisomer. The low yields reported [1] and our previous results on the cycloaddition reactions of nitrile oxides with tropone prompted us to reinvestigate this reaction.[2] Tropone is in fact a suitable model for studying regioselectivity and periselectivity in the same molecule.

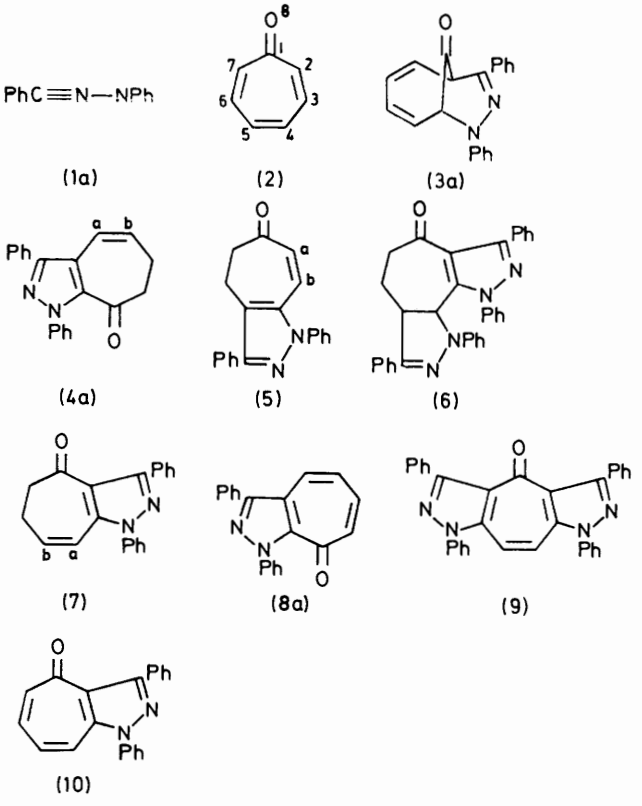
We also report the results of the reaction of the dipole (1a) with tricarbonyltroponeiron. The 1,3-dipolarophilic reactivity of the latter has been explored only with diazoalkanes.[3]

RESULTS

Diphenylnitrilimine (1a), prepared *in situ* by the action of triethylamine on *N*-α-chlorobenzylidene-*N'*-phenylhydrazine in anhydrous benzene at room temperature, was treated with an excess of tropone (2). Compounds (3a) (5.0%), (4a) (6.0%), (5) (5.0%), (6) (1.5%), (7) (37.0%), (8a) (trace), (9) (2.0%), and (10) (20.0%) were isolated. With the sole exception of the cycloadduct (3a), the isolated monoadducts were derived from the primary adducts either by loss or by transposition of two hydrogen atoms.

The structure of the adduct (3a), already established by Houk, was confirmed by his ready (high yield) and selective transformation into compounds (4a) and (8a) through an initial [1,5] sigmatropic rearrangement to the (11a) (not isolated) (Scheme). Such a transformation takes place only slowly in benzene at room temperature, but can be brought about in *ca.* 5 h by heating under reflux in the same solvent. A faster (3.5 h) reaction with the same results was obtained in boiling ethanol. The possibility of a retro-cycloaddition [(3a) ⟶ (1a) + (2)] at least in part responsible for the above described processes was ruled out by the observation that compounds (4a) and (8a) were the sole products obtained on heating (3a) in norbornene at 130 °C; no traces of the (1a)–norbornene adduct were detected.

At this point, however, it should be made clear that compound (4a) is a primary product of the reaction of



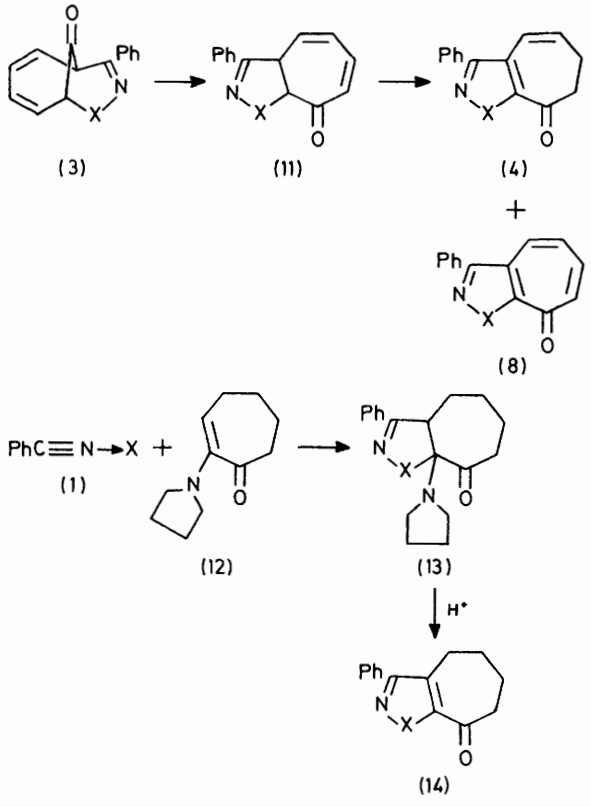
(1a) with tropone, and is not derived from (3a). This was ascertained by a careful study of the behaviour of (3a) under the reaction conditions and during work-up of the products. Furthermore, t.l.c. showed that the ratio of (3a) to (4a) (*ca.* 1 : 1) was constant throughout the reaction time. The intrinsic interest of this sigmatropic transposition led us to study also the behaviour

[1] K. N. Houk and C. R. Watts, *Tetrahedron Letters*, 1970, 4025.

[2] C. De Micheli, R. Gandolfi, and P. Grünanger, *Tetrahedron*, 1974, **30**, 3765.

[3] M. Frank-Neumann and D. Martina, *Tetrahedron Letters*, 1975, 1759.

of the oxygen analogue (3b) under various conditions (Scheme). This adduct was stable at room temperature in the solid state and in solution (several solvents), but was converted on heating for 4.5 h in benzene at 125 °C



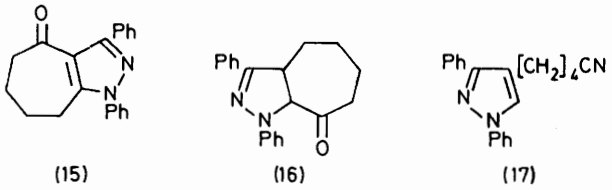
a; X = NPh b; X = O

SCHEME

partly into the isoxazole (4b) and partly into benzonitrile and tropolone. The formation of the latter two products parallels the behaviour of 5-acyl-Δ^2-isoxazolines, which smoothly give rise to nitriles and α-diketones.[4] When compound (3b) was heated in ethanol (3.5 h; 125 °C), the isoxazole (4b) was the sole product.

Catalytic hydrogenation of compounds (4) and (8) [to (14)] and of (7) and (10) (major constituents of the reaction mixture) [to (15)] verified the structural assignments (Scheme). Compounds (14) were also obtained from the regiospecific cycloaddition of the 1,3-dipoles with the monoenamine (12) from cycloheptane-1,2-dione, followed by acid-induced elimination of the base from the adducts (13) * (Scheme). The assumption of regiospecificity of the above mentioned reactions is based on the many reported examples of cycloadditions of nitrile oxides and nitrile imides with enamines which, with no exceptions, gave Δ^2-isoxazolines and Δ^2-pyrazolines with the base at position 5 of the heterocycle.

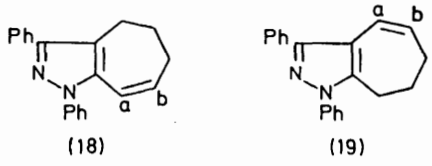
To ascertain the regiochemistry of compounds (7) and (10), compound (14a) was also prepared by oxidation of (16) with chloranil. Compound (16) is the major component obtained, together with (15) and traces of (14a), from the reaction of diphenylnitrilimine (1a) with cyclohept-2-enone. The structure (16) was assigned on the basis of n.m.r. data (H-5 of the pyrazoline ring resonated at low field value as a doublet, and H-4 gave rise to a complex multiplet) and on transformation into the nitrile (17) on treatment of the corresponding oxime with phosphorus pentachloride in ether. The pyrazole proton of compound (17) absorbed in the aromatic region, $\delta > 7.20$, as expected for H-5; H-4 in pyrazoles generally absorbs at $\delta < 7.0$ whereas the H-5 signal generally appears at $\delta > 7.0$ [5] [*e.g.* for 1,3-diphenylpyrazole H-5 resonates at $\delta > 7.30$, whereas H-4 absorbs at δ 6.75 (solvent $CDCl_3$; $J_{4,5}$ 2.5 Hz)].



Furthermore, the absence of n.m.r. signals characteristic of α- and β-protons of αβ-unsaturated ketones allowed the determination of the position of the double bond in structures (4) and (7). In conclusion the main product isolated in this work and that reported by Houk [1] are the same, and the correct structure is (7) and not (4a).

The structure of compound (5) was established on the basis of its catalytic reduction to a dihydro-derivative with a carbonyl stretching absorption at 1 700 cm^{-1}, and Wolff–Kishner reduction to (18), which was alternatively synthesized from the tosylhydrazone of compound (14a) by treatment with sodium glycolate.

In attempts to synthesize compounds (18) and (19) by Wolff–Kishner reduction of compounds (4a) and (7)



a mixture of (18) and (19) was obtained in both cases. As compounds (18) and (19) are stable under the reaction conditions, we offer no explanation at present for the observed reciprocal isomerization.

The formation of the bis-adducts (6) and (9) in the reaction of diphenylnitrilimine (1a) with tropone (2) is due to further regiospecific cycloadditions of diphenylnitrilimine (1a) with the monoadducts (7) and (10), respectively, as proved by their independent synthesis from the 1,3-dipole and the monoadducts. Assignment of structures (6) and (9) is based on ^1H n.m.r. evidence:

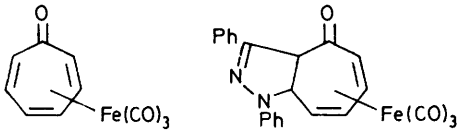
* The regioisomer of (14b) has already been fully characterized.[2]

[4] G. Bianchi, A. Gamba, and R. Gandolfi, *J.C.S. Perkin I*, 1974, 1757.

[5] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' Pergamon, Oxford, 1969, p. 209.

the vinyl protons of (9) resonate as a singlet, and the pyrazoline protons of (6) are characterized by notably different chemical shifts. [The pyrazoline isomeric with (6) which could be formed from the reaction of (1a) and (7) should have pyrazoline protons with similar chemical shifts.[2]]

The reaction of diphenylnitrilimine (1a) with tricarbonyltroponeiron (20) gave (21) * as the predominant



(20) (21)

adduct with little of its regioisomer. The products were converted by cerium(IV) into compounds (10) and (8a) [ratio of (10) to (8a) 17 : 1] *via* prior oxidation of the pyrazoline ring.

The dipolarophilic reactivities of tropone and tricarbonyltroponeiron have been compared by treating diphenylnitrilimine (1a) with a mixture of the two dipolarophiles [ratio (2) : (20) 3 : 1] in large excess. A mixture of the adduct (21) and its regioisomer and the adduct (10) was obtained in the ratio [(21) + regioisomer] : (10) 2.7 : 1, which shows the greater reactivity of the tricarbonyliron complex. Remarkably, compound (7) was not formed in the latter reaction, showing that oxidation of the primary adduct to (10) in this case prevails over the potentially competing hydrogen atom transposition.

DISCUSSION

A detailed discussion of factors influencing reactivity, regioselectivity, and periselectivity in the 1,3-dipolar cycloadditions of nitrile oxides with tropone has been reported.[2] The results of the present work show that with nitrile imides as well as with nitrile oxides [2] and diazoalkanes,[6] the reactivity of the 2,3-double bond of tropone is higher than that of the 4,5-double bond, and that the $[_{\pi}4_s + _{\pi}2_s]$ prevails over the competitive $[_{\pi}6_s + _{\pi}4_s]$ cycloaddition. Furthermore, the formation and isolation of the adduct (5) appears to be the first unambiguous example of the dipolarophilic reactivity of the 4,5-double bond of tropone with 1,3-dipoles.[7]

In contrast to nitrile oxides, nitrile imides do not react with the carbonyl group of tropone; they do however react with the 2,3-double bond to give both possible regioisomers (4a) and (7), the latter being predominant. The adduct (7) possesses the same regiochemistry as found for the sole adduct obtained from the reaction of nitrile oxides with tropone (2).

Frontier orbital energies and coefficients should provide explanations of the reported results. Unfortunately only the HOMO energy value (ionisation potential 8.90 eV) [8] and the calculated frontier orbital coefficients (LUMO: c_8 0.00, c_1 0.00, c_2 0.521, c_3 −0.232; HOMO: c_8 0.653, c_1 −0.187, c_2 −0.393, c_3 −0.093) [9] of tropone are known. Though frontier orbital coefficients of diphenylnitrilimine are not available, a reasonable qualitative estimate (based on calculated data for the parent 1,3-dipole $CH\equiv\overset{+}{N}-\bar{N}-H$) gives the coefficient at the carbon atom a smaller value in the HOMO and a much larger value in the LUMO than the corresponding coefficients at the nitrogen atom at the other end of the 1,3-dipole.[10,11]

Hence, if, as expected, regiochemistry in this reaction is mainly determined by frontier orbital interactions, the results show a dominant $LUMO_{nitrilimine}$–$HOMO_{tropone}$ [favouring adduct (7)] interaction, even if the other interaction, $HOMO_{nitrilimine}$–$LUMO_{tropone}$ [favouring adduct (4a)], is also operating.

The relatively moderate $LUMO_{nitrilimine}$–$HOMO_{tropone}$ interaction, in comparison with the analogous benzonitrile oxide–tropone system, can be considered the main cause of the non observance of dipolarophilic activity of the carbonyl group, as the $HOMO_{nitrilimine}$–$LUMO_{tropone}$ interaction shows little perturbability at that part of the dipolarophile.

The data obtained from the reaction of tricarbonyltroponeiron suggest that the cycloaddition is LUMO-dipole controlled, with stronger interaction between position 2 of the dipolarophile and the carbon end of the 1,3-dipole. In addition, steric factors work in the same direction: the well known larger steric requirement of the PhC end of diphenylnitrilimine (1a) [12] and the bulky dienetricarbonyliron group [13] make (21) more favoured than its regioisomer.

We believe that the [1,5] sigmatropic rearrangement of compounds (3) takes place in a concerted way. As suggested by the negligible effect of solvent on the reaction rate, a dipolar intermediate is improbable. Furthermore the fact that the [1,5] rearrangement was the sole transposition observed, with no [1,3] process occurring seems to rule out possibility of a diradical intermediate. Several examples of ready [1,5] migration involving sp^2 carbon atoms of carbonyl, vinyl, and phenyl groups are known, but few cases have been reported involving nitrogen and oxygen atoms.[14] The

* An *anti*-relationship of the pyrazoline ring with respect to the $Fe(CO)_3$ group seems the most probable for compound (21).[3]

[6] M. Frank-Neumann, *Tetrahedron Letters*, 1970, 2143; L. J. Luskus and K. N. Houk, *ibid.*, 1972, 1925; M. Frank-Neumann, and D. Martina, *ibid.*, 1975, 1755.

[7] Y. Fujise, H. Saito, and S. Ito, *Tetrahedron Letters*, 1976, 1117.

[8] J. C. Bünzii, D. C. Frost, and C. Weiler, *J. Amer. Chem. Soc.*, 1974, **96**, 1952; C. Muller, A. Schweig, and H. Vermeeer, *Angew. Chem. Internat. Edn.*, 1974, **13**, 273.

[9] L. Salem, *J. Amer. Chem. Soc.*, 1968, **90**, 553.

[10] K. N. Houk, J. Sims, R. E. Duk, R. W. Strozier, and J. K. George, *J. Amer. Chem. Soc.*, 1973, **95**, 7287.

[11] K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Amer. Chem. Soc.*, 1973, **95**, 7301.

[12] R. Huisgen, *Angew. Chem. Internat. Edn.*, 1963, **2**, 565 and 633.

[13] R. P. Dodge, *J. Amer. Chem. Soc.*, 1964, **86**, 5429.

[14] C. W. Spangler. *Chem. Rev.*, 1976, **76**, 187; L. A. Paquette, *Angew. Chem. Internat. Edn.*, 1971, **10**, 11; F. G. Klarner and E. Vogel, *ibid.*, 1973, **12**, 840; D. M. Jerime, B. Witkop, C. L. McIntosh, and O. L. Chapman, *J. Amer. Chem. Soc.*, 1974, **96**, 5578; R. A. Abramovitch and I. Sinkai, *Accounts Chem. Res.*, 1976, **9**, 192.

[1,5] sigmatropic rearrangements studied here show unambiguously that an sp^2 carbon atom is a migration centre superior to oxygen or nitrogen.

Finally we note that $[{}_{\pi}6_s + {}_{\pi}4_s]$ tropone–diene adducts on heating do not undergo sigmatropic transposition (involving an sp^3 carbon centre) but retro-cycloaddition processes.[15]

EXPERIMENTAL

I.r. spectra were obtained for Nujol suspensions with a Perkin-Elmer 257 spectrophotometer. N.m.r. spectra (60 MHz) were recorded at 36 °C with a Perkin-Elmer R12 spectrometer (Me_4Si as internal standard; solvent $CDCl_3$). T.l.c. was performed on plates pre-coated with silica gel GF_{254} (Merck) and preparative column chromatography with silica gel H (Merck) (elution with cyclohexane–ethyl acetate and benzene–ethyl acetate mixtures in various proportions).

Physical, analytical, and i.r. data are given in the Table.

Reaction of Diphenylnitrilimine (1a) *with Tropone* (2).—A solution of *N*-α-chlorobenzilidene-*N'*-phenylhydrazine (3.00 g, 13.0 mmol), triethylamine (3.00 ml, 21.0 mmol), and a large excess of tropone (15.0 g, 141 mmol) in anhydrous benzene (80 ml) was left in the dark at room temperature for 50 h. The precipitated triethylamine hydrochloride was filtered off and the solution washed several times with water (to remove unchanged tropone), dried, and evaporated. The residue was separated by column chromatography to give, in order of elution, the primary adduct (3a), 6,7-*dihydro*-1,3-*diphenylcycloheptapyrazole*-8(1H)-*one* (4a), 4,5-*dihydro*-1,3-*diphenylcycloheptapyrazol*-6(1H)-*one* (5), 1,5,6,6a,9,9a-*hexahydro*-1,3,7,9-*tetraphenylcyclohepta*[2,1-c:3,4-c']*dipyrazol*-4-*one* (6), 5,6-*dihydro*-1,3-*diphenylcycloheptapyrazol*-4(1H)-*one* (7), 1,3-*diphenylcycloheptapyrazol*-8(1H)-*one* (8), 1,7-*dihydro*-1,3,5,7-*tetraphenylcyclohepta*[1,2-c:5,4-c']*dipyrazol*-4-*one* (9), and 1,3-*diphenylcycloheptapyrazol*-4(1H)-*one* (10) (yields are given in the Results section) and small amounts of a compound affording colourless needles from cyclohexane–benzene, m.p. 169—171 °C, not further characterized.

N.m.r. data: (4a), δ 6.69 (1 H, d, H_a, J_{ab} 11.0 Hz), 6.26 (1 H, m, H_b), and 2.90—2.25 (4 H, m, $CH_2{\cdot}CH_2$); (5), δ 7.03 (1 H, d, H_a, J_{ab} 12.3 Hz), 6.12 (1 H, d, H_b), and 3.20—2.70 (4 H, m, $CH_2{\cdot}CH_2$); (6), δ 5.14 (1 H, d, H-5 of pyrazolidine, $J_{4,5}$ 9.3 Hz), and 4.00 (m, H-4 of pyrazoline); (7); δ 6.50—6.30 (2 H, m, H_a and H_b) and 2.90—2.30 (4 H, m, $CH_2{\cdot}CH_2$); (8a), δ 8.00—6.50 (m, aromatic and vinyl protons); (9), δ 7.06 (2 H, s, vinyl protons); (10), δ 7.90—6.50 (m, aromatic and vinyl protons); for n.m.r. spectrum of (3a) see ref. 1.

A mixture of compound (3a), triethylamine, triethylamine hydrochloride, and tropone in anhydrous benzene was left at room temperature for 60 h. The same work-up as described above gave compounds (3a) (90%) and (4a) (trace amounts).

The reaction of (1a) with an equimolar amount of (7) or (10) in anhydrous benzene at room temperature gave compounds (6) (77%) and (9) (52%), respectively, as the only isolated adducts.

Thermal Rearrangement of Compound (3a).—A solution of compound (3a) (30 mg) in anhydrous benzene (5 ml) was heated under reflux until complete disappearance of starting material was shown by t.l.c. (5.0 h). Column chromatography gave compounds (4a) (70%) and (8a) (15%).

The rearrangement of (3a) in refluxing ethanol proceeded to completion in 3.5 h (t.l.c.) to give compound (4a) (65%) and a trace of (8a).

The results of heating (3a) in norbornene for 30 min at 130 °C are given in the Results section.

Thermal Rearrangement of Compound (3b).—A solution of compound (3b) (40 mg) in anhydrous benzene (5 ml) was heated in a stainless steel bomb in an oil-bath at 125 °C for 4.5 h. The components were detected (and in one instance isolated) as follows: 6,7-*dihydro*-3-*phenylcyclohept*[d]*isoxazol*-8-*one* (4b) (pure compound; 40%) by column chromatography; benzonitrile by i.r. and g.l.c. techniques and odour; tropolone by t.l.c. and by the formation of an

Physical, analytical, and i.r. data for compounds (3)—(21)

Compound	Cryst. solvent	M.p. (°C)	Found (%) C	H	N	Formula	Required (%) C	H	N	$\nu_{max.}$/cm^{-1} (C=O)
(3a)	MeOH [a,b]	111—112	80.2	5.5	9.6	$C_{20}H_{16}N_2O$	80.0	5.4	9.3	1 739
(4a)	MeOH [b,c]	158—159	80.1	5.6	9.5					1 670
(4b)	EtOH [d]	129—130	75.1	5.1	6.3	$C_{14}H_{11}NO_2$	74.7	4.9	6.2	1 675
(5)	MeOH [b,d]	141—142	79.7	5.4	9.8	$C_{20}H_{16}N_2O$	80.0	5.4	9.3	1 652
(6)	AcOEt [a]	269—271	80.2	5.4	11.5	$C_{33}H_{26}N_4O$	80.1	5.3	11.3	1 680
(7)	MeOH [e]	188—189	80.3	5.7	9.1	$C_{20}H_{16}N_2O$	80.0	5.4	9.3	1 665
(8a)	MeOH [b,e]	224—225	80.9	4.8	9.6	$C_{20}H_{14}N_2O$	80.5	4.7	9.4	1 590
(9)	C_6H_6–AcOEt [a]	281—283	80.3	4.8	11.3	$C_{33}H_{24}N_4O$	80.5	4.9	11.4	1 635
(10)	EtOH [c]	183—184	80.8	4.8	9.6	$C_{20}H_{14}N_2O$	80.5	4.7	9.4	1 605
(12)	(Oil) [f,h]		73.4	9.2	7.6	$C_{11}H_{17}NO$	73.7	9.6	7.8	1 675
(13b)	EtOH [e]	178—180	72.1	7.3	9.1	$C_{18}H_{22}N_2O_2$	72.5	7.4	9.4	1 722
(14b)	Cyclohexane [c]	101—102	73.8	5.4	6.0	$C_{14}H_{13}NO_2$	74.0	5.8	6.2	1 660
(14a)	MeOH [e]	165—166	79.5	5.9	9.2	$C_{20}H_{18}N_2O$	79.4	6.0	9.3	1 673
(15)	EtOH [d]	129—131	78.9	6.0	9.2					1 672
(16)	EtOH [e,h]	147—148	79.0	6.8	9.4	$C_{20}H_{20}N_2O$	78.9	6.6	3.2	1 722
(17)	EtOH [e]	104—106	79.8	6.5	14.1	$C_{20}H_{19}N_3$	79.7	6.4	14.0	*i*
(18)	Petroleum [a]	89—90	83.6	6.1	9.6	$C_{20}H_{18}N_2$	83.9	6.3	9.8	
(19)	EtOH [d]	110—112	83.4	6.5	9.9					
(21)	MeOH [a,g]	155—157	62.5	3.4	6.6	$C_{23}H_{16}FeN_2O_4$	62.8	3.7	6.4	1 641 [j]

[a] Prisms. [b] Pale yellow. [c] Leaflets. [d] Plates. [e] Needles. [f] B.p. 104—106 °C at 0.6 mmHg. [g] Orange-yellow. [h] Yellow. [i] $\nu_{max.}$ 2 240 cm^{-1} (C≡N). [j] $\nu_{max.}$ 2 070, 2 000, and 1 990 cm^{-1} [$Fe(CO)_3$].

[15] R. C. Cookson, B. V. Drake, J. Hudec, and A. Morrison, *Chem. Comm.*, 1966, 15; S. Ito, K. Sakan, and Y. Fujise, *Tetrahedron Letters*, 1970, 2873; K. N. Houk and R. B. Woodward, *J. Amer. Chem. Soc.*, 1970, **92**, 4145; K. N. Houk and D. J. Northington, *ibid.*, 1971, **93**, 6694.

intense deep green colour with an excess of iron(III) chloride; [16] and (3b), traces, by t.l.c. G.l.c. analysis of the crude material gave a ratio of (4b) to benzonitrile of 9 : 1.

An unidentified oily product ($\nu_{max.}$ 1 685 cm^{-1}) was also isolated in small amounts by column chromatography. Thermal rearrangement of (3b) in ethanol (125 °C; 3.5 h) gave as sole product compound (4b) (70%).

N.m.r. data of (4b): δ 6.60—6.40 (2 H, m, vinyl protons) and 3.30—2.30 (4 H, m, $CH_2 \cdot CH_2$).

2-Pyrrolidin-1-ylcyclohept-2-enone (12).—A mixture of cycloheptane-1,2-dione (5.0 g), pyrrolidine (2.5 g), and toluene-*p*-sulphonic acid (50 mg) in anhydrous benzene (25 ml) was heated under reflux with separation of the water formed (*ca.* 30 min). After removal of the benzene, the product was obtained by distillation at reduced pressure as a yellow oil (60%).

4,5,6,7-Tetrahydro-1,3-diphenylcycloheptapyrazol-8(1H)-one (14a).—A solution of *N*-α-chlorobenzylidene-*N'*-phenylhydrazine (0.39 g), triethylamine (0.25 ml), and 2-pyrrolidinocyclohept-2-enone (0.30 g) in anhydrous benzene (20 ml) was left at room temperature for 2 days. The usual work-up gave an oily residue which was treated with ethanol (6 ml) and concentrated hydrochloric acid (0.5 ml) to give the pure *product* (14a) (55%) (collected by filtration). T.l.c. showed that compound (15) was not present in the ethanolic mother liquors.

Compound (14a) was also obtained, in quantitative yield, by heating the adduct (16) with an equimolar amount of chloranil in toluene for 6 h.

4,5,6,7-Tetrahydro-3-phenylcyclohept[d]*isoxazol-8-one* (14b).—A solution of benzohydroximoyl chloride (0.30 g) in anhydrous benzene (15 ml) was added dropwise at room temperature during 2 h to a stirred solution of triethylamine (0.3 ml) and the adduct (12) (0.31 g) in the same solvent (15 ml). The resulting mixture was set aside for 48 h. *3a,4,5,6,7,8a-Hexahydro-3-phenyl-8a-pyrrolidin-1-ylcyclohept*[d]*isoxazol-8-one* (13b) (0.46 g, 89%) was isolated and purified by crystallisation from ethanol. A mixture of (13b) (200 mg) and 10% sulphuric acid (20 ml) was heated under reflux for 6 h, cooled, poured into water, and extracted with ether to give the *product* (14b) (73%).

Reaction of Diphenylnitrilimine (1a) *with Cyclohept-2-enone.*—A solution of *N*-α-chlorobenzylidene-*N'*-phenylhydrazine (2.0 g), cyclohept-2-enone (1.20 g), and triethylamine (1.3 ml) in anhydrous benzene (20 ml) was left at room temperature for 15 days. The usual work-up gave a residue which was chromatographed to yield (in the following order) *3a,4,5,6,7,8a-hexahydro-1,3-diphenylcycloheptapyrazol-8(1H)-one* (16) (1.37 g, 52%) [δ 4.68 (1 H, d, H-5 of pyrazoline, $J_{4,5}$ 12.6), 4.05 (1 H, m, H-4)], compound (14a) (0.065 g, 2.5%), and *5,6,7,8-tetrahydro-1,3-diphenylcycloheptapyrazol-4(1H)-one* (15) (0.609 g, 23%).

5-(1,3-Diphenylpyrazol-4-yl)pentanenitrile (17).—The oxime of the ketone (16), m.p. 185—195 °C, was obtained in high yield by heating a solution of (16) and a two-fold excess of hydroxylamine hydrochloride and anhydrous sodium acetate in 95% ethanol.

An excess of phosphorus pentachloride (1.3 g) was added to a cooled, stirred solution of the oxime (0.983 g) in absolute ether (80 ml), which was then left at room temperature for 2 days. The mixture was poured over crushed ice and the organic layer separated, washed with water, dried, and evaporated to give the *nitrile* (17) (0.86 g, 92%); δ 7.90—7.20 (11 H, m, aromatic), 2.70 (2 H, m, CH_2), 2.23 (2 H, m, CH_2), and 1.70 (4 H, m, $CH_2 \cdot CH_2$).

Catalytic Hydrogenation of Compounds (4), (7), (8), *and* (10).—Compounds (4a), (4b), (7), (8a), and (10) (100 mg) were separately dissolved in ethanol (95%; 10 ml) and catalytically reduced with hydrogen over palladium–carbon (5%; 15 mg) at 760 Torr and room temperature. After an uptake of 1.0 [2.0 in the cases of (8a) and (10)] equiv. the reaction was interrupted, and the solution filtered and evaporated under reduced pressure. The crude products were purified by column chromatography or by crystallisation from appropriate solvents to give pure compounds (14a), (14b), or (15) (70—95% yields).

Catalytic Hydrogenation of Compound (5).—Compound (5) (100 mg) was dissolved in ethanol (95%; 10 ml) and catalytically reduced with hydrogen over palladium–carbon (5%; 15 mg) at 760 Torr and room temperature. After uptake of 0.8 equiv. the reaction was interrupted and the solution filtered and evaporated. The residue was separated by column chromatography to give compound (5) (21 mg) and two dihydro-derivatives. The component with higher R_F (37 mg; 41%) gave needles (from light petroleum), m.p. 136—137 °C (Found: C, 79.2; H, 6.2; N, 9.6. Calc. for $C_{20}H_{18}N_2O$: C, 79.4; H, 6.0; N, 9.3%); $\nu_{max.}$ 1 700 cm^{-1} (C=O). The second dihydro-derivative (25 mg; 27.5%) gave plates (from ethanol), m.p. 149—150 °C (Found: C, 79.3; H, 6.3; N, 9.1%); $\nu_{max.}$ 3 280 cm^{-1} (OH); this compound was also obtained in quantitative yield by reduction of (5) in methanol with sodium borohydride.

Wolff–Kishner Reduction of Compounds (4a), (5), *and* (7).—A mixture of compound (4a), (5), or (7) (50 mg), 85% hydrazine hydrate (0.4 ml) and ethylene glycol (3 ml) was heated under reflux for 45 min. Then potassium hydroxide (0.30 g) in water (0.5 ml) was added; after refluxing for 30 min the condenser was removed until the temperature of the solution had reached 185—190 °C; then refluxing was continued for 1 h. The mixture was cooled, diluted with water, and extracted with ether. Products were separated by column chromatography (cyclohexane–ethyl acetate, 19 : 1). From compound (5) only *1,4,5,6-tetrahydro-1,3-diphenylcycloheptapyrazole* (18) (74%) was obtained; (4a) and (7) gave mixtures of (18) and its *1,6,7,8-tetrahydro-isomer* (19) (8 and 70%, and 41 and 49%, respectively). N.m.r. data: (18), δ 6.28 (1 H, m, H_a, J_{ab} 12.0 Hz) and 5.83 (1 H, m, H_b); (19), δ 6.42 (1 H, m, H_a, J_{ab} 11.7 Hz) and 5.68 (1 H, m, H_b).

Synthesis of Compounds (18) *and* (19).—The tosylhydrazone of the ketone (14a), m.p. 184—186 °C [or of (15), m.p. 210—213 °C] was prepared by prolonged heating (5 days) of a solution of (14a) [or of (15)] and an equimolar amount of tosylhydrazine in ethanol. A solution of the tosylhydrazone of (14a) (0.10 g) [or of the tosylhydrazone of (15)] in 2N-sodium glycolate (2.0 ml) was heated at 120 °C for 1 h. After cooling the mixture was poured into water and extracted with ether. Evaporation gave compound (18) [or (19)] which was purified by column chromatography. T.l.c. showed that the alternative isomer (19) [or (18)] was not formed in the reaction.

Reaction of Diphenylnitrilimine (1a) *with Tricarbonyltroponeiron* (20).—A solution of *N*-α-chlorobenzylidene-*N'*-phenylhydrazine (0.46 g, 2.0 mmol), triethylamine (20% excess), and tricarbonyltroponeiron (20) [17] (0.49 g, 2.0

[16] J. W. Cook, A. R. Gibb, R. A. Raphael, and A. R. Somerville, *J. Chem. Soc.*, 1951, 503.

[17] D. F. Hunt, G. C. Farrant, and G. T. Rodeheaver, *J. Organometallic Chem.*, 1972, **38**, 349.

mmol) in anhydrous benzene (15 ml) was left in the dark at room temperature for 5 days; then t.l.c. showed the total disappearance of starting material (20). Column chromatography gave a product (0.79 g, 90%) homogeneous on t.l.c. in several solvent systems whose n.m.r. spectrum [δ 5.80—5.15 (3 H, m, H-5 of pyrazoline and two vinyl protons), 4.01 (1 H, d, H-4 of pyrazoline, $J_{4,5}$ 9.3 Hz), and 3.30—2.85 (2 H, m, vinyl protons)] was consistent with structure (21). However the product was shown to be a mixture of (21) and its regioisomer by reaction with cerium(IV) (following experiment).

Oxidation of Compound (21) *and its Regioisomer with Cerium*(IV).—To a stirred mixture of cerium(IV) ammonium nitrate (1.63 g) and anhydrous disodium hydrogen phosphate (0.71 g) in acetone (20 ml) was added to a solution of the crude product (0.40 g) obtained from the reaction of (1a) with (20) in acetone (10 ml) over 30 min. The mixture was left at room temperature for 48 h, then diluted with water and extracted with ether. The solvent was removed and the residue separated by column chromatography to give compounds (10) (0.159 g, 53%) and (8a) (9.0 mg, 3.0%). In a parallel experiment the oxidation mixture was maintained at 0 °C throughout the addition period (30 min) and for an additional 1 h. Then the whole was worked up as described above and the residue was chromatographed to give compounds (8a) and (10) and a mixture of their tricarbonyliron complexes (25%). Only *tricarbonyl*-[1,3-*diphenylcycloheptapyrazol*-4(1H)-*one*]*iron*, the major component of the mixture of two complexes, was isolated in a pure state, by crystallisation from methanol as yellow needles, m.p. 165—166 °C (Found: C, 63.3; H, 3.1; N, 6.1. $C_{23}H_{14}FeN_2O_4$ requires C, 63.0; H, 3.2; N, 6.4%); $\nu_{max.}$ 1 633 cm^{-1} (C=O), 2 070, 2 000, and 1 990 cm^{-1} [$Fe(CO)_3$]; δ 6.22 (2 H, m) and 3.34 (2 H, m).

Competitive Reaction of Compounds (2) *and* (20).—A solution of *N*-α-chlorobenzylidene-*N'*-phenylhydrazine (150 mg, 0.65 mmol), tropone (415 mg, 3.9 mmol), tricarbonyltroponeiron (319 mg, 1.3 mmol), and triethylamine (0.11 ml) in anhydrous benzene was left in the dark at room temperature for 24 h. The precipitated triethylamine hydrochloride was filtered off, the solution evaporated under reduced pressure, and the residue chromatographed to give, in order of elution compound (21) and its regioisomer (191 mg, 67%), tricarbonyltroponeiron, the adduct (10) (49 mg, 25%), and tropone. Traces of other products were present (t.l.c.) but not isolated in a pure state.

We thank Professor G. Bianchi for discussions and the C.N.R. (Rome) for financial support.

[6/1578 *Received*, 11*th August*, 1976]