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REACTIONS OF CYCLOPROPENES WITH NITRILE OXIDES AND NITRILE IMINES

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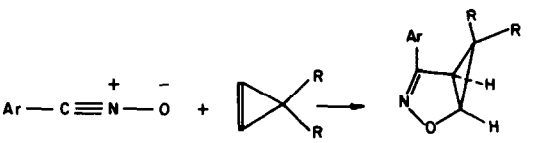
Although cyclopropenes are known to be reactive dienophiles in the Diels-Alder reaction[1], little attention has been paid so far to their reactivity on dipolarophiles in 1,3-dipolar additions; only some reactions with diazo compounds[2] and azides[3] have been reported.

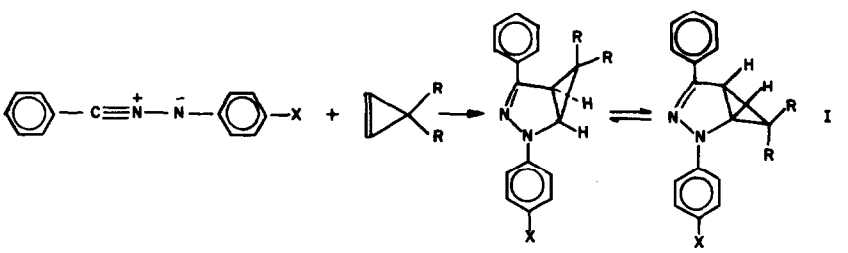
This paper gives a brief account of the reactions of cyclopropene and 3,3-dimethylcyclopropene with nitrile oxides and nitrile imines. The two cyclopropenes rapidly reacted with nitrile oxides to give virtually quantitative yields of the corresponding bicyclic adducts.



R=R=H
R=R=CH_3

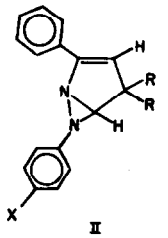
The NMR spectra of the products, featuring non-equivalent R groups, were independent of temperature up to 180 °C.

A similar 1,3-dipolar addition was observed with nitrile imines (prepared in situ from the corresponding hydrazonic acid chlorides and triethylamine). The adducts were obtained in good yields. They displayed ring inversion, manifested by line broadening and coalescence of the R absorptions in their NMR spectra at increased temperatures.

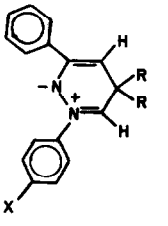


Two likely mechanisms can be formulated to explain this ring inversion:

(1) A mechanism analogous to that of the degenerate vinylcyclopropane rearrangement[4], involving II as the intermediate.



II



III

(2) A mechanism involving an azomethine imine (III) as the intermediate, formally analogous to the norcaradiene-cycloheptatriene equilibrium. The formation of III may well be favoured by the presence at the three-membered ring of an electron-donating and an electron-accepting group.

On the basis of the following reasoning we tentatively conclude that the reaction proceeds via intermediate III. The results of NMR kinetic measurements (Table) show that replacement of X = H by NO_2 caused a substantial decrease in the rate of ring inversion. This demonstrates, although indirectly, that the presence of an adjacent electron-releasing nitrogen atom is essential for ring inversion. Moreover, the nitrile oxide adducts, which, instead of this nitrogen have an oxygen atom, with a far smaller capacity to donate electrons, displayed no ring inversion at temperatures up to 180 °C.

The low activation energy of the ring-inversion process seems not consistent with the value one would expect for a vinylcyclopropane rearrangement in general.

The absence of significant solvent- and R-substituent effects is not in conflict with our conclusion. These effects, consequently, do not allow of any differentiation between the two mechanisms.

KINETIC AND THERMODYNAMIC DATA ON THE RING INVERSION OF I

Compounds I with		Solvent	$\Delta\nu$ [a]	$T_{coalescence}$	k 10 °C	ΔH^*	ΔS^*	ΔG^*_{Tc}
X	R		Hz	°C	s^{-1}	kcal/mol	e.u.	kcal/mol
H	H	$CDCl_3$	100	-20				12
NO_2	H	"	92	55				16
H	CH_3	toluene[b]	33	-18.5	410	8.5	-17	12.7
H	CH_3	$CDCl_3$[b]	64	-16	950	9.8	-10	12.5
H	CH_3	o-dichlorobenzene	60	-17.5				12.4
NO_2	CH_3	toluene[b]	43.5	54	5.5	11.5	-14	16.2
NO_2	CH_3	$CDCl_3$[b]	64	64	2.6	13.4	-9	16.5
NO_2	CH_3	CD_3NO_2	65	59	3.0	14.4	-6	16.3
NO_2	CH_3	CD_3COOH	63	55				16

a. $\Delta\nu = \nu_{R\text{-exo}} - \nu_{R\text{-endo}}$; measurements were performed on a Varian HA-100 spectrometer.

b. rates were determined over a temperature range of from 40 °C below to 40 °C above the the coalescence temperature.

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