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LASER INDUCED SYNTHESIS: CONDENSATION OF ACRYLONITRILE ON MESITYL OXIDE

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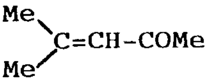
ABSTRACT

The photoaddition of acrylonitrile to mesityl oxide was accomplished at 355 nm with high quantum yield (15%) using a pulsed laser (intensity= 9 MW/cm^2, pulse duration= 13 ns, repetition rate= 10Hz) and selectively led to three products in contrast to irradiation with a mercury lamp which principally gave an acrylonitrile polymer and with continuous wave laser (intensity= 5.7 W/cm^2) which gave a much lower quantum yield (0.4%).

Certain terpenic compounds with a nitrile function have been referred to as "green note" derivatives in the recent literature (1). Their potential interest to the perfumery industry led us to investigate their photochemical synthesis. To begin with, attention was directed to the possibility of reaction between a simple substrate, mesityl oxide (I), and a simple reagent, acrylonitrile (II).

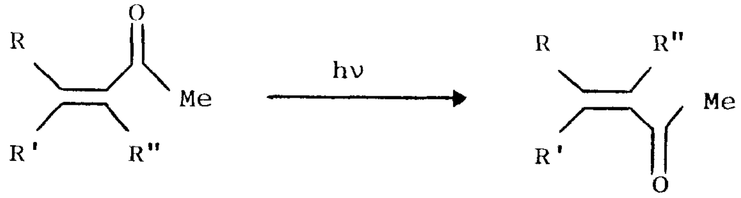


I

$CH_2=CH-C\equiv N$

II

In classical photochemistry, however, i.e. when mercury vapour lamps are used as the source of irradiation, acrylonitrile generally results in dimers (2,3) or undergoes rapid polymerization (4) that is a very serious obstacle to its use as a reagent. In the case of photocycloadditions on substituted cyclohexenones, for example, acrylonitrile polymers predominate at the expense of cycloadducts (5). On the other hand as for the most of the acyclic enones, the primary photochemical reaction of mesityl oxide is a cis-trans isomerization around the double bond (6).



There are also reports of deconjugations displacing the double bond in the β,γ position of the carbonyl function (7,8). So an intermolecular reaction seems unfavourable with regard to intramolecular processes. It is for this reason that examples of cycloadducts are only found with cyclic enones.

Classical photochemistry was thus predictably unsatisfactory for our purpose. Nevertheless, the reactivity of acrylonitrile already observed with laser irradiation of limonene (9) encouraged us to undertake the study of the reaction between mesityl oxide and acrylonitrile with this kind of source and to compare the results with those provided by a standard mercury vapour lamp.

The emissions employed were those given by a Nd-YAG laser and frequency tripler crystals at 355 nm and CW Ar+ laser at 351.1 nm, in other words such as to excite α,β-ethylenic ketones by means of their n-π* transition (4).

RESULTS AND DISCUSSION

Pulsed laser irradiation of a solution of mesityl oxide in acrylonitrile (see experimental part) resulted in the appearance of three addition products. This occurs in a selective fashion, since no dimers were detected on analysis and no polymers were observed (absence of the characteristic white mass).

CW laser irradiation and HP mercury lamp irradiation led to the same three addition products. In this last case, however, substantial polymerization acrylonitrile was responsible for rapid setting of the irradiated solution.

The experimental conditions and parameter values for the three reactions are shown in the following table:

Light source	concentration of mesityl oxide in acrylonitrile	Quantum yield
Nd-YAG laser (355 nm)	20 %	15 %
CW Ar+ laser (351,1 nm)	20 %	0.4 %
High pressure mercury lamp	20 %	0.2 %*

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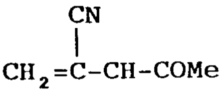
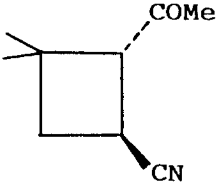
*Minimum value (an unknown part of the photons is used for polymerization).

Both GC/MS and silica column chromatography followed by NMR of ^{1}H and ^{13}C suggested that the addition products had the foll structures:

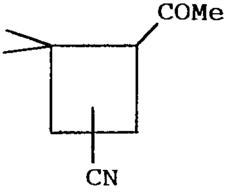


$$CH_2{=}\overset{\overset{\displaystyle CN}{|}}{C}{-}CH{-}COMe$$

A



B



C

In the experiments, the relative percentages for the three compounds (calculated from the peak areas in GPC) were of the orders of 5% (A), 50% (B) and 45% (C).

The reaction is quasi quantitative (Chemical yield= 98%) when irradiation duration is sufficient; the photoproducts are not degradable therefore at 355 nm because of, certainly, the disappearance of conjugation in their structure responsible of absorption of mesityl oxide at this wavelength.

Comparison of the quantum yields clearly shows the important part played by the light source. We can see that no acrylonitrile polymerization is detectable in the case of laser irradiation by contrast with lamp irradiation, but that high quantum yield is only reached with pulsed laser.

The laser monochromaticity compared with the broad band emission of HP lamp can explain the absence of polymer: excitation is then selective vis-à-vis the conjugated ketone and acrylonitrile remains in the fundamental state and cannot polymerize. Except a small discrepancy in the wavelengths, the difference between the two lasers lies in the value of the intensity and its temporal dependance owing, particularly, the possibility of multi-step absorption processes with the pulsed laser(10). Taken as a whole, therefore, our observations suggest that the formation of addition products obtained with the CW laser and the high-pressure mercury lamp can be attributed to a monophotonic process (excited mesityl oxide plus acrylonitrile in the ground state). To this should be added multiphotonic processes when the pulsed laser is used, as has been proposed in the photocyclization of carvone (11).

A more precise definition of these mechanisms must undoubtedly be worked out. The fact remains, however, that there is an undeniable difference between the patterns obtained with the pulsed laser as opposed to the other sources. This finding, coupled with the observation that the products are obtained selectively with the pulsed laser, with a high quantum yield which allows a fast reaction and quasi quantitatively (98%) when irradiation duration is sufficient, indicates that this approach could well be extended to more complex molecules, particularly the terpenic ketones or aldehydes, in relation to the "green notes" mentioned earlier.

Moreover, the use of cyclic α,β-ethylenic ketones avoids the parasite cis-trans isomerization around the double bond, owing to the rigidity of the cycle, and thus opens the way to even higher yields. Preliminary assays now in progress with carvone are in line with this view and suggest the possibility of rapid quantitative reactions using a flow system.

EXPERIMENTAL PART

* Laser irradiations: conducted on 3 ml of cooled solution, with the beam entering the open upper surface of a 1 cm Ø cylindrical cell.
Sources: Nd-YAG laser (λ= 355 nm, intensity= 9 MW/cm^2, pulse duration= 13 ns, repetition rate= 10 Hz), CW Ar+ laser (λ= 351.1 nm, intensity= 5.7 W/cm^2).

* Lamp irradiations: conducted on 200 ml of cooled solution in a reactor housing the high pressure mercury-vapour lamp: Heraeus TQ 150 Z2.

* Mass spectra were obtained by GC/MS coupling. Separation on a silica column with the aid of an 80:20 eluting mixture of cyclohexane and ethyl acetate gave product B in the pure state, whereas products A and C were not completely pure.

Product A: MS m/z 136(100); 43(94,4); 109(19,3); 151(15,1); 94(9,1); 83(8,4); 53(9,0); 67(4,8). ^{1}H NMR shows two vinylic protons at 4,4 and 4,6 ppm.
Product B: MS m/z 43(100); 56(82,2); 96(24,8); 108(13,3); 83(11,0); 67(3,9); 151(2,3).
NMR ^{13}C (CDCL3) δ= 203 ppm($\underline{C}{=}O$); 120($\underline{C}{\equiv}N$); 58,7($\underline{C}{-}H$); 15,8($\underline{C}{-}H$); 38,5(Me2$\underline{C}$); 36,1($\underline{C}$H2); 29,8($\underline{C}$H3); 29,0($\underline{C}$H3); 21,9($\underline{C}$H3).
NMR ^{1}H δ=0,9 ppm(s,3H,$\underline{C}$H3); 1,3(s,3H,$\underline{C}$H3); 2,01(s,3H,$\underline{C}$H3); 2(d,1H,X portion of ABXY multiplet, H of CH2); 1,99(d,1H,Y portion of ABXY multiplet, J(YA)=8,6 Hz, H of CH2); 3,27(multiplet,1H,A portion of ABXY multiplet, J(AB)trans= 7,04 Hz, J(AX)=8,6 Hz, C$\underline{H}$-CN); 3,27 ppm(d,1H,B portion of ABXY multiplet, J(BX)=J(BY)=0 Hz, C$\underline{H}$-COCH3).

Product C: Mass spectrum presents the same peaks as that of product B with only slight differences in intensity. This product was not obtained in a pure state.

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