October, 1988] © *1988 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn., 61, 3731—3732 (1988)* 3731

A Michael Reaction Product of Cyclohexylidenemalononitrile

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(Received March 31, 1988)

Synopsis. Cyclohexylidenemalononitriles dimerize and cyclize to give 3-amino-2,4-dicyano-2-[imino(methoxy)-methyl]spiro[bicyclo[4,4,0]deca-3,5-diene-1,1′-cyclohexane] (**3**). The crystal structure of **3** was determined by an X-ray diffraction method.

Alkylidenecyanoacetates and cyclohexanone undergo a Michael reaction to give cyclization products.[1)] We investigated similar Michael-type cycloaddition reactions of alkylidenemalononitriles using sodium methoxide, and found that acyclic alkylidenemalononitriles dimerized and cyclized to give 2-azabicyclo[2.2.2]-octadiene derivatives (**1**)[2)] whose crystal structure could be determined by an X-ray diffraction method, as shown in Fig. 1.[3)] The bridged compounds release alkene to give pyridine derivertives. Contrary to acyclic compounds, cyclohexylidenemalononitrile was found to give an imidate derivertive **3** which was different from expected bridged compounds (Fig. 2). We report here the results of an X-ray crystal diffraction of **3**.

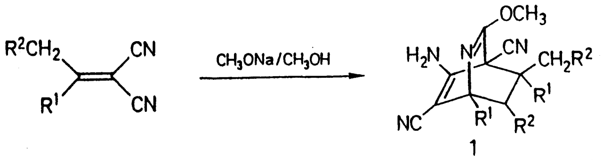

Fig. 1. Reactions of acyclic alkylidenemalononitliles.

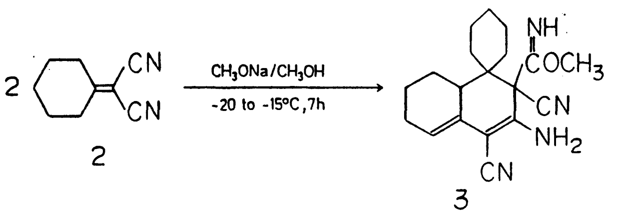

Fig. 2. Reaction of cyclohexylidenemalononitrile.

Experimental

Cyclohexylidene malononitriles were obtained according to usual Knoevenagel reaction procedure. Sodium methoxide was purchased from Kanto Chemical, and methanol was dried with magnesium methoxide.

Preparation of 3. To a solution of cyclohexylidenemalononitrile (2.92 g, 0.02 mol) in methanol (20 ml) was added sodium methoxide (0.54 g, 0.01 mol) at 5—7 °C with stirring. Stirring was continued for 6 h and then the reaction mixture was left for 6 h at 5—7 °C. The precipitate formed was filtered, washed with cold methanol, dried in vacuo, and recrystallized from acetone to give 0.9 g (yield 30%) of **3** (mp 227—230 °C. Found: C, 69.99; H, 7.35; N, 16.97%. Calcd for $C_{19}H_{24}N_4O$: C, 70.34; H, 7.46; N, 17.27%).

X-Ray Crystallography. A single crystal obtained from ethanol with approximate dimensions of 0.30×0.25×0.43 mm was used for data collection. The crystal data are as follows; $C_{19}H_{24}N_4O$, M_w=324.2, monoclinic, $P2_1/c$, a=16.141 (2), b=9.078(1), c=11.942(2) Å, β=100.45(2)°, U=1720.8(5) Å^3, Z=4, D_x=1.252 g cm^{-3}, D_m=1.258 g cm^{-3}, μ(Mo $K\alpha$)=0.867 cm^{-1}. The crystal was mounted on a Rigaku AFC 5R diffractometer at Institute for Molecular Science and intensity data were collected up to 2θ=60° with graphite monochromated Mo $K\alpha$ radiation. Unit cell parameters were determined by a least-squares refinement from setting angles of 42 accurately adjusted reflections ($27\leq2\theta\leq41°$). In total, 2670 reflections ($|F_o|>2.5\sigma(F_o)$) out of 5480 independent reflections ($0\leq h\leq22$, $0\leq k\leq12$, $-16\leq l\leq16$) were used for the refinement. Three standard reflections were measured at every 100 reflections, and no significant deterioration was observed. Lorentz and polarization corrections were applied. Subsequent calculations were carried out using a universal program (UNICS III)[4)] at Institute for Molecular Science and at the University of Tokyo. The structure was solved by a direct method. All the non-hydrogen atoms appeared and almost all the inter-peak distances were reasonable. The refinements were carried out by a block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen atoms. All the hydrogen atoms were located on the difference Fourier Maps and were refined isotropically to final R values

Table 1. Final Atomic Parameters with Estimated Stadard Deviations

Atom	X	Y	Z	B_{eq}
O	5651(1)	402(3)	2257(2)	3.3
N(1)	5386(2)	1753(3)	−247(3)	3.9
N(2)	6613(2)	−1447(3)	2563(2)	3.4
N(3)	6444(2)	−1470(3)	−402(2)	3.1
N(4)	8384(2)	−2724(4)	−924(3)	4.7
C(1)	8497(2)	−70(3)	1242(3)	2.5
C(2)	9324(2)	−160(4)	1207(4)	4.1
C(3)	9987(2)	565(5)	2065(5)	5.4
C(4)	9654(2)	917(5)	3140(4)	4.9
C(5)	8837(2)	1788(4)	2825(3)	3.3
C(6)	8150(2)	847(3)	2103(2)	2.3
C(7)	7358(2)	1708(3)	1498(2)	1.9
C(8)	6671(2)	465(3)	1049(2)	1.9
C(9)	7020(2)	−700(3)	329(2)	2.0
C(10)	7866(2)	−883(3)	436(2)	2.3
C(11)	7523(2)	2585(3)	444(2)	2.3
C(12)	7899(3)	4116(4)	648(3)	4.3
C(13)	7420(3)	5047(4)	1375(4)	4.9
C(14)	7368(2)	4277(4)	2485(3)	3.6
C(15)	6979(2)	2739(3)	2300(2)	2.7
C(16)	5941(2)	1186(3)	318(2)	2.4
C(17)	6328(2)	−317(3)	2033(2)	2.3
C(18)	5253(3)	−223(5)	3140(4)	5.0
C(19)	8160(2)	−1924(3)	−315(3)	3.0

Positional parameters are multiplied by 10**4. Thermal parameters are given by the equivalent temperature factors (A**2).

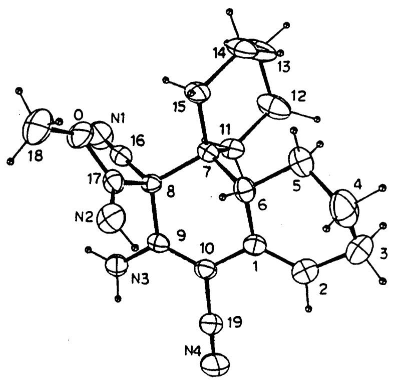

Fig. 3. Perspective view of **3** and the numbering of the atoms.

0.060[R_w=0.088, $w=1/(3.0+0.01|F_o|^2)$ for $|F_o|<15$ and $w=1/(\sigma^2(F_o)+0.0013|F_o|^2)$ for $|F_o|\geq 15$]. There was no residual peak greater than 0.7 e Å^{-3}.

Table 1 lists the non-hydrogen atomic coordinates with equivalent isotropic temperature factors.[5]

Results and Discussion

Molecular Structure. A perspective view of **3** is shown in Fig. 3. Table 2 lists selected bond distances and angles. We expected that **3** is a bridged compound, as described earlier,[2] on the basis of ^{1}H NMR spectra. Contrary to our expectation, it had a free imidate and a double bond instead of a bridged structure. We could not find any remarkable structural characteristics that favor a bicyclo compound instead of a bridged structure and stabilize the imidate group. The bond distances, C(17)-N(2) and O-C(17), are rather shorter than usual C-N double bond and C-O single bond, respectively. Thus, electrophilicity of C(17) should be rather small. A cyclohexane ring attaches perpendiculary to an almost planar hexalin system. The bond distances, C(7)-C(8) and C(8)-C(9), are elongated, probably due to a steric interaction among the substitutents. Other bond distances and angles are all normal. We are investigating similar reactions for other cycloalkylidenemalononitriles; their results will be reported elsewhere.

Table 2. Bond Distances and Angles with Estimated Standard Deviations

Atom	Distance/Å	Atom	Distance/Å
O-C(17)	1.341(4)	N(2)-C(17)	1.249(4)
N(3)-C(9)	1.348(4)	C(1)-C(2)	1.345(5)
C(1)-C(10)	1.467(4)	C(7)-C(8)	1.605(4)
C(8)-C(9)	1.533(4)	C(9)-C(10)	1.358(4)
	Angle/degree		Angle/degree
O-C(17)-N(2)	122.5(3)	C(7)-C(8)-C(9)	111.7(2)
O-C(17)-C(8)	110.0(2)	C(7)-C(8)-C(17)	112.7(2)
N(2)-C(17)-C(8)	127.3(3)	C(16)-C(8)-C(17)	106.9(2)

References

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3) Y. Nakano, M. Igarashi, and S. Sato, *Acta Crystallogr., Sect. C*, **43**, 738 (1987).

4) T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res.*, **55**, 69 (1979).

5) The F_o-F_c table, anisotropic temperature facters, hydrogen positional parameters, isotropic thermal parameters, data of possible hydrogen bonds, and non-essential bond distances and angle are kept as Document No. 8840 at the Chemical Society of Japan.