added dropwise with constant stirring. The hydrazones immediately dissolved, and the bromides precipitated out in 80–85% yields after 10–30 min, the time depending mainly on the reactivity of the DNPs. In the case of hydrazidoyl bromides **6n–p**, usually a 4-fold excess of bromine was used, and, after 4 h of stirring, the solution was warmed on a sand bath. The hydrazidoyl bromides thus obtained were separated from the solution, washed with a little acetic acid and then with petroleum ether, and recrystallized from appropriate solvents (Table I).

***Hydrazidoyl Bromides* 6q–t.** Hydrazones **5q–t** (0.04 mol) were added to a mixture of 200 mL of glacial acetic acid and 120 mL of acetic anhydride containing sodium acetate (27 g), and the temperature was lowered to 0–5 °C by means of an ice-salt bath. To this was added over a 1-h period bromine (0.04 mL) dissolved in 5 mL of acetic acid. After additional stirring for 3 h, the solution was poured into 2 L of water. A yellow product so obtained was stirred for some time and then left overnight at room temperature. The product was filtered, washed with water, and dried under vacuum. The products so obtained were generally crystallized from alcohol or aqueous alcohol.

Acknowledgment

We thank the Director, H.B.T.I., Kanpur, for providing facilities.

Literature Cited

(1) Wiley, R. H.; Knabeschuh, L. H. *J. Org. Chem.* **1953**, *18*, 836.
(2) Huisgen, R.; Grashey, R.; Laur, P.; Leitermann, H. *Angew. Chem.* **1960**, *72*, 416.
(3) Huisgen, R. *Proc. Chem. Soc., London* **1961**, 357.
(4) Acheson, R. M.; Hole, F. *J. Chem. Soc.* **1962**, 748.
(5) Cloris, J. S.; Eckell, A.; Huisgen, R.; Wallbillich, G.; Weberndoerfer, B. *Chem. Ber.* **1967**, *100*, 1593.
(6) Huisgen, R.; Seidel, M.; Sauer, J.; McFarland, J. W.; Wallbillich, G. *J. Org. Chem.* **1959**, *24*, 892.
(7) Huisgen, R.; Sauer, J.; Sturm, H. J.; Markgraf, J. H. *Chem. Ber.* **1960**, *93*, 2106.
(8) Chattaway, F. D.; Walker, A. J. *J. Chem. Soc.* **1925**, 127.
(9) Lozinskii, M. O.; Lapatinskaya, N. A.; Pelkis, P. S. *Zh. Org. Khim.* **1965**, *1*, 1877.
(10) Barnish, I. T.; Gibson, M. S. *Chem. Commun.* **1967**, 1001.
(11) Pechmann, V. H. *Chem. Ber.* **1894**, *27*, 320.
(12) Dieckmann, W.; Platz, L. *Chem. Ber.* **1905**, *38*, 2987.
(13) Burgess, J. M.; Gilson, M. S. *Tetrahedron* **1962**, *18*, 1001.
(14) Chattaway, F. D.; Daldy, F. G. *J. Chem. Soc.* **1928**, 2760.
(15) Ross, A.; Ring, R. N. *J. Org. Chem.* **1961**, *26*, 579.
(16) Chattaway, F. D.; Adamson, A. B. *J. Chem. Soc.* **1933**, 840.
(17) Hegarty, A. F.; Scott, F. L. *Tetrahedron Lett.* **1965**, 3801.
(18) Vogel, A. I. "Practical Organic Chemistry", 3rd ed.; Longman: London, 1973; pp 346.

Received for review September 26, 1980. Revised Manuscript Received June 8, 1981. Accepted July 22, 1981. P.P. thanks C.S.I.R., New Delhi, for the award of J.R.F.

Synthesis of 2,2-Disubstituted 5-Cyanocyclopentanones and Comparison of Their Enol Contents with the Corresponding Cyclohexanones

Stuart S. Kulp* and Jeffrey D. Lipko

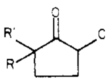
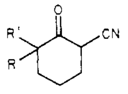
Department of Chemistry, Moravian College, Bethlehem, Pennsylvania 18018

The enol contents of 14 2,2-disubstituted 5-cyanocyclopentanones and the analogous 2,2-disubstituted 6-cyanocyclohexanones are reported. The Brown–Brewster–Schechter prediction of less enolization for the five-membered alicyclics vs. the six-membered analogues is valid for all but three cases (Ph, *i*-C_3H_7; Ph, CH_2Ph; Ph, *n*-C_4H_9).

We previously reported (*2*) the development of a procedure for determining the percent enol for 2-cyanocyclohexanones by an infrared technique. Using this method for 14 compounds in the cyclohexanone series and 7 analogous compounds, which were available to us, in the cyclopentanone series (*3*, *4*) gave data which led to a correlation attempt via the Brown–Brewster–Schechter proposal (*5*) to exo/endo bonds in five- or six-membered rings. The rule predicts less enolization in the five-membered compounds.

We now report the synthesis of the remaining seven 2,2-disubstituted 5-cyanocyclopentanones and their enol contents as well as the necessary 1-cyano-2-methoxy-3,3-disubstituted cyclopentenes (H, H; Me, Me; Ph, *n*-C_5H_{11}; Ph, Ph) employed as conjugated nitrile standards.

Table I. Percent Enol of 2-Cyanocyclohexanones and 2-Cyanocyclopentanones in Dioxane

substituents		mol % enol	
R	R′		
H	H	1	37
Et	Et	2	18
Me	Me	4	20
C_6H_5	*i*-butyl	6	6
C_6H_5	*i*-propyl	6	5
C_6H_5	Et	6	10
C_6H_5	cyclohexyl	6	6
C_6H_5	*n*-amyl	7	10
C_6H_5	$CH_2C_6H_5$	8	4
C_6H_5	*n*-propyl	8	10
C_6H_5	*n*-butyl	8	5
C_6H_5	C_6H_5	9	24
C_6H_5	$(CH_2)_2C_6H_5$	13	13
C_6H_5	Me	13	19

Absorption of the keto nitriles in dioxane at 2210 cm^{-1} (conjugated CN) gave the concentration of the enol form by reference to a calibration plot for a related 1-cyano-2-meth-

0021-9568/81/1726-0420$01.25/0

Table II. Boiling Points or Melting Points (°C) of Compounds I-IV

substituents compd	I	II	III	IV
CH_3	145 (1 mm)	157 (1 mm)	mp 90-91	145 (1 mm)
C_3H_7	140-143 (1 mm)	mp 71.5-73.5	mp 143-144.5	140 (1 mm)
C_4H_9	180-181 (1 mm)	172-173 (1 mm)	mp 96-98	180 (1 mm)
i-C_4H_9	163-165 (1 mm)	165-168 (1 mm)	mp 92.5-93.5	165 (1 mm)
C_5H_{11}	159-160 (1 mm)	173-178 (1 mm)	175-180 (1 mm)	160 (1 mm)
$PhCH_2$	mp 109.5-110.5	180-190 (1 mm)	mp 141-142	mp 109.5-110.5
$PhCH_2CH_2$	185-187 (1 mm)	220-222 (2 mm)	mp 103.5-104.5	187 (1 mm)

oxycycloalkene. The cyclopentanone compounds are arranged in increasing percent enol in Table I. Replicate determinations were ±0.3% in five of six cases and ±0.8% for the exception.

The infrared method was substantially superior to the NMR method when applied to this problem.

The percent enol for the cyclopentanones range from 1 to 13%, and for the cyclohexanones they range from 4 to 37%. The largest difference is in the first entry—the unsubstituted 2-cyanocycloalkanones, i.e., 1% vs. 37%. In the cyclopentanone series the lower enol values tend to be related to symmetry of identical simple substituents.

Comparison of enolization of the five-membered compounds with their six-membered analogues generally supports the Brown prediction. There are three exceptions according to this data, but the differences are not striking.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Section Model 237B instrument. NMR spectra were obtained on a Perkin-Elmer R24 instrument. Elemental analyses were by G. I. Robertson Laboratory, Florham Park, NJ, and were submitted to the editor. All spectra were consistent with the assigned structures, and representative curves will be published in the Sadtler Series at a later date. 1-Methyl-3-*p*-tolyltriazene was purchased from Willow Brook Laboratories, Inc., P.O. Box 526, Waukesha, WI 53186.

Synthetic Sequence. The additional cyclopentanones required for this study were synthesized via the previously described (*3*) sequence; i.e., alkylation of the appropriate alkylphenylacetonitrile with 1-bromo-3-chloropropane to the 5-chloro-2-alkyl-2-phenylpentanenitrile (I) → 2-alkyl-2-phenylhexanedinitrile (II) → 2-alkyl-2-phenyl-5-cyanocyclopentanonimine ($\rightleftharpoons$ enamine tautomer) (III) → 2-alkyl-2-phenyl-5-cyanocyclopentanone (IV). Although several of the precursor compounds in this sequence were previously reported (*6*), we found some differences in properties and have listed all additional compounds prepared in our work. The boiling points or melting points are listed in Table II.

1-Cyano-2-methoxycyclopentenes. Equimolar quantities of the 2-cyanocyclopentanones and 1-methyl-3-*p*-tolyltriazene were dissolved separately in ether. Slow addition of the ketone usually evolved nitrogen. When gas evolution was not spontaneous, the mixture was refluxed for 10-30 min. The mixture stood overnight, and then 10% HCl was added. Further washes with dilute NaOH and then water were followed by drying ($MgSO_4$). After being filtered, the solution was concentrated. Liquids were purified by distillation and solids by recrystallization from 50% ethanol. Pure products were obtained in 50-80% yields. The parent compound had bp 101-104 °C (25 mm). The 3,3-disubstituted compounds were as follows: CH_3, CH_3 (bp 123-128 °C (1 mm)); Ph, n-C_5H_{11} (bp 160-166 °C (5 mm)); Ph, Ph (mp 118-119 °C). These compounds were utilized as the calibration standards as previously described (*2*) for the four types of cyclopentanones: H, H; alkyl, alkyl; phenyl, alkyl; and diphenyl.

Determination of Enols. The previously described procedure was utilized (*2*).

Literature Cited

(1) Lipko, J. D. "Senior Honors Paper"; Moravian College, Bethlehem, PA, 1976.

(2) Kulp, S. S.; Schmoyer, R. W.; Freeze, D. E.; Buzas, J. *J. Org. Chem.* **1975**, *40*, 453.

(3) Kulp, S. S.; Fish, V. B.; Easton, N. R. *Can. J. Chem.* **1965**, *43*, 2512.

(4) Kulp, S. S.; Molnar, J.; Miller, P. J.; Herman, S. T. *J. Org. Chem.* **1971**, *36*, 2203.

(5) Brown, H. C.; Brewster, J. H.; Schechter, H. *J. Am. Chem. Soc.* **1954**, *76*, 467.

(6) Salmon-Legagneur, F.; Rabadeux, J. *C. R. Hebd. Seances Acad. Sci.* **1965**, *261*, 5524.

Received for review January 5, 1981. Accepted April 27, 1981.

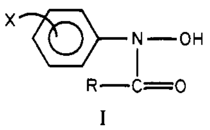
Preparation and Properties of *N*-Arylhydroxamic Acids[†]

Vettithara C. Koshy and Shiv G. Tandon*

Department of Chemistry, Ravishankar University, Raipur 492.010, India

Thirteen new *N*-substituted hydroxamic acids were prepared by the acylation of *N*-arylhydroxylamine with appropriate acid chloride at low temperature in ethereal solutions containing a suspension of sodium bicarbonate. The yields range from 40% to 90%. These compounds were characterized in terms of elemental analyses, melting points, and ultraviolet and infrared spectra.

The chemistry of hydroxamic acid has been of considerable interest to this research group since 1960 (*1*). Over this period the preparation and the properties of more than 200 hydroxamic acids were reported (*2*-*13*). The present investigation deals with the preparation and the properties of 13 *N*-arylhydroxamic acids, I



I

[†] Part of the Ph.D. Thesis of V.C.K., Ravishankar University, Raipur, India, 1981.

0021-9568/81/1726-0421$01.25/0