vapor phase chromatograms and nmr spectra (for CH_3OH) and comparison with those of known samples of HCN, HN_3, and CH_3OH. To a sample in concentrated NH_3 was added a known excess of KCN, and the excess was titrated with a standard silver solution as in the Ni determination. From the percentage nickel and the known amount of added CN^-, the CN^- arising from the complex could be determined.

Anal. Calcd for $Ni(C_2H_3N_4)_2$: Ni, 26.1; CN^-, 23.2. Found: Ni, 26.3; CN^-, 23.4.

The tetrazolylnickel when wet decomposes rapidly in the atmosphere, but when dry decomposition is slow. The compound has appreciable solubility only in dimethyl sulfoxide in which a blue solution forms. Further studies of these solutions are in progress. If treated with nitromethane a new green substance forms which appears to be a disolvate.

Anal. Calcd for $Ni(C_2H_3N_4)_2 \cdot 2CH_3NO_2$: Ni, 16.9. Found: Ni, 17.1.

The tetrazolylnickel decomposes rapidly in concentrated NH_3 (see above) and in acid solutions, in which some HCN, HN_3, and CH_3OH are formed, but mostly the products are Ni^{2+} and 1-methyltetrazole. The complex decomposes more slowly in contact with neutral solutions. It explodes upon being heated in a flame.

Magnetic susceptibility was measured by the Gouy method, with $Hg[Co(SCN)_4]$ as a standard; μ_{eff} was 2.90 BM. The moment was corrected for the diamagnetism of the ligand by use of Pascal's constants. The spin-only value for $3d^8$ is 2.83.

The electronic spectrum of the solid was obtained by use of a Beckman, Model DK-2, spectrophotometer and diffuse reflectance attachment and showed absorptions at 8.06×10^3, 14.7×10^3, a shoulder at 25.0×10^3, and a large (charge transfer) band at 30.9×10^3 cm^{-1}. If the maximum, which gives rise to the shoulder, was between 27 and 28 $\times 10^3$ cm^{-1}, the spectral pattern would correspond to octahedral nickel, and the two d–d transitions would correspond to ${}^3A_{2g}$–${}^3T_{2g}(F)$ and A_{2g}–${}^3T_{1g}(F)$.

Infrared spectra were measured in Nujol and Fluorolube mulls and in KBr disks and were measured on a Unicam SP-200 spectrometer. Far-infrared spectra were measured in Nujol mulls between CsBr and polyethylene plates on a Perkin-Elmer Model 301 spectrometer. In the main, the features of the tetrazole are retained but with changes in intensities and position of the absorptions.

Several important features should be pointed out here. Absorptions at 590 and 485 cm^{-1} are present in the complex and not in the free tetrazole and may be attributed to the Ni–C–N bend and to the Ni–C stretch, respectively. The Ni–C stretch[4] in $Ni(CN)_4{}^{2-}$ is found at 543 and the bend at 433 and 421 cm^{-1}, and the Fe–C stretch[5] in $Fe(CN)_6{}^{4-}$ is found at 416 and the bend at 583 cm^{-1}. A band is found only in the complex at 2150 cm^{-1} which is some 20–50 cm^{-1} higher than the C–N stretch in first-row transition element cyanides, but is probably the C–N stretch. A band occurs at 298 cm^{-1} which can probably be attributed to an Ni–N bond[6,7] by analogy to nickel pyridine and pentamethylenetetrazole complexes.

It seems likely that the complex is polymeric because of the low solubility in most solvents, the probable presence of both Ni–C and Ni–N bonds, and the octahedral configuration, which seems likely for the nickel from the electronic spectrum. The tetrazole ring seems to be intact in the complex, if we consider the over-all infrared spectrum and the recovery of most of the free tetrazole, when the compound is decomposed in acid. Since the ring is broken in concentrated NH_3 between the 1 and 5 positions and the 3 and 4 positions to give cyanide ion and ultimately methanol and azide, it appears that the 1–5 N–C and 3–4 N–N bonds may be rather ionic. The 5–4 C–N bond must be much more like the bond in cyano complexes and less like the C–N in the free tetrazole.

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An Interesting Yield Increase in the Formation of Cyclic Acyloins

Sir:

The extensive use of the acyloin condensation, especially for the synthesis of medium rings, has stimulated surprisingly little systematic study.[1] Good evidence for the radical nature of the heterogeneous reaction has been provided, but this work has not been continued.[2,3] There is also one report of the optimum, reproducible yields of cyclic product in the medium ring series.[4] This work reported over-all yields of cyclic ketones based on diester and suggested the necessity of the present study.

It was our desire to obtain relative rates of cyclization for the dimethyl esters of the nine- to fourteen-carbon dicarboxylic acids. As a first step we determined the approximate length of time required for the complete disappearance of the ester. These results are given in Table I.

Table I. Time Required for the Complete Consumption of Ester in the Heterogeneous Acyloin Condensation

Ester (dimethyl)	Time, min
Nonanedioate	480
Decanedioate	180
Undecanedioate	165
Dodecanedioate	60
Tetradecanedioate	30

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These reactions, as well as the others reported here, were carried out essentially by the method of Allinger[5] except that 0.01 mole of each diester was used in a microscale apparatus. Only relative amounts of acyloin and the principal by-product, the 1,2-diketone, were determined. For the medium rings the ratio of acyloin to diketone was remarkably constant at 3:1. With the two large rings it changed abruptly to 5:1.

Two hours was selected as the standard reaction time. The yields of cyclization products under these standard conditions were determined for each of the individual diesters. Because of the present uncertainty concerning the exact relationship between acyloin and diketone yields, we propose in this preliminary communication to discuss only the sum of the yields of these two monocyclic products. Table II presents the yields for individual diesters.

Table II. Yield of Cyclization Products as a Function of Chain Length

Ester (dimethyl)	Yield, %
Nonanedioate	16
Decanedioate	52
Undecanedioate	69
Dodecanedioate	72
Tridecanedioate	64
Tetradecanedioate	84

It is clear that the reaction time employed is well below the optimum. When the reaction of dimethyl nonanedioate was conducted under our conditions for 7 hr, the yield of 2-hydroxycyclononanone was 48% (lit.[6] 42%).

The procedure for determining relative rates of cyclization was just as described for the individual compounds except that 0.01 mole of each diester was added, *i.e.*, the total ester concentration was doubled. The yields of nine-membered cyclic products are given in Table III and those of the higher homologs in Table IV.

Table III. Yield of C$_9$ Cyclization Products in the Presence of Homologous Reactants in Equimolar Quantities

Homologous ester (dimethyl)	Yield of C$_9$ products, %
Nonanedioate (standard)	16
Decanedioate	52
Undecanedioate	60
Dodecanedioate	57
Tridecanedioate	62
Tetradecanedioate	58

All of the yield values reported in this communication were determined using gas chromatography. Measurements for representative runs were duplicated and determined on two different columns. All values are the average of at least three individual sample measurements. In all cases the agreement between values was better than 3%.

The most outstanding observation in our attempted determination of relative rates is the 3–4-fold increase in the yield of nine-membered cyclic products when the reaction was carried out in the presence of an homologous diester. A second fact which can be seen in these data is the marked alternation for both the nine-membered cyclization products and the homologs prepared in their presence. Those higher homologs which cause the smallest increase in nine-membered products are converted to cyclic products in higher yield than when they were run separately. Just the opposite is true of those homologs which cause the greatest increase in yield of C$_9$ products. While the magnitude of the changes in yield observed here are not as spectacular as the increase in yield of C$_9$ products, the analytical method employed (glpc) leaves no doubt that they are significantly greater than experimental error.

Table IV. Yield of Homologous Cyclization Products in the Presence of Dimethyl Nonanedioate in Equimolar Quantity

Ester (dimethyl)	Yield of cyclization products, %
Decanedioate	69
Undecanedioate	62
Dodecanedioate	84
Tridecanedioate	52
Tetradecanedioate	87

We have been unable to find any previous report of an effect of the type described here. While the observations in this communication are consistent with Prelog's proposal for the unique effectiveness of the acyloin condensation for the synthesis of medium carbocyclic systems,[7,8] any extensive speculation on the mechanistic details would be unwise until at least some of the numerous experiments which suggest themselves are carried out. Two of these have been attempted in a preliminary fashion. In the first case an equimolar amount of methyl hexanoate was added and a slight increase in the yield of nine-membered cyclization products did result (22%). In another experiment, the concentration of the C$_9$ diester was doubled. Nearly the same amount of starting material was recovered as at the lower concentration (61% at 0.01 mole and 66% at 0.02 mole), but the yield of cyclization products dropped sharply to 5%.

There is a superficial similarity between our observations and those of Walling in the relative reactivities of hydrocarbons toward alkoxy radicals.[9] While the two studies deal with quite different situations, the observed results from both serve to emphasize the ever present dangers in obtaining and interpreting data for relative reactivities.

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