FORMATION PATHWAYS AND STRUCTURE–PROPERTY INTERRELATIONSHIP OF 3-IMINO-1-METHYL-5,5-DIALKYL-4,7,7-TRICYANO-2-OXABICYCLO-[2.2.1]HEPTANE DERIVATIVES*

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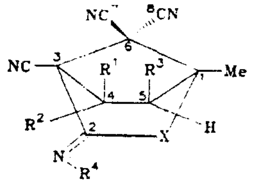
UDC 547.828'514.3:541.634:543.422:548.737

The problems of the structure–property interrelationship of 3-imino-2-oxabicyclo[2.2.1]heptane derivatives are discussed on the basis of x-ray diffraction studies (XDS). A pathway for the formation of the bicyclic compounds is proposed, and the realization of spirans in the reaction of sym-tetracyanoethane with conjugated cyclic systems containing s-cis C=C and C=O fragments is substantiated. The factors responsible for the syn orientation of the oxygen atom and the N-substituent of the imino group are analyzed. It is shown that a change in the steric hindrance in the bicyclic compounds leads to a change in the conformation of the latter. The reasons for the shortening of the C_{sp^3}–C_{sp^3}, C_{sp^3}–C_{sp}, *and C=N exo bonds and the correlation of the XDS and IR spectroscopic data are examined. From the XDS data for N-bromo-substituted imines, a model for* $Br^+ ... N{\equiv}C$ *electrophilic attack was proposed*

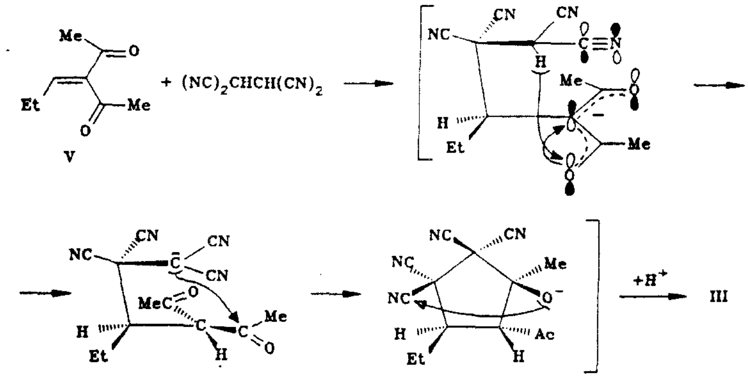
The synthesis, spectral and structural evidence for the structure, and a probable pathway for the formation of bicyclic imino esters I and II [2, 3] from 1,1,2,2-tetracyanoethane and s-cis-α,β-unsaturated ketones [2, 3] have been previously reported. In the present research, on the basis of data from an x-ray diffraction analysis of I-IV and qualitative MO theory we established a pathway for the formation of the bicyclic imino esters, analyzed their structures, studied the stereochemistry of the bromination of imino ester I, and determined the structural aspect of the electrophilic addition of bromine to the C≡N bond.†



I–IV

I X=O, $R^1=R^2=Me$, $R^3=R^4=H$; II X=O, $R^1=R^2=Me$, $R^3=H$, $R^4=Br$; III X=O, $R^1=R^4=H$, $R^2=Et$, $R^3=Ac$; IV $X=N-NEt_2$, $R^1=R^2=Me$, $R^3=R^4=H$

Compound III was synthesized from propylideneacetylacetone (V) and tetracyanoethane, while IV was synthesized from mesityl oxide diethylhydrazone and tetracyanoethane. The structures of oxabicycloheptane derivatives III and IV were established by x-ray diffraction analysis (Figs. 1 and 2). The stable conformation of starting enone V requires maximal π–π* conjugation vis-à-vis minimal steric hindrance, which automatically leads to s-cis and s-trans orientations of the acetyl groups. The tetracyanoethane anion adds to the ketone at the C_β atom, since, first, the lowest vacant



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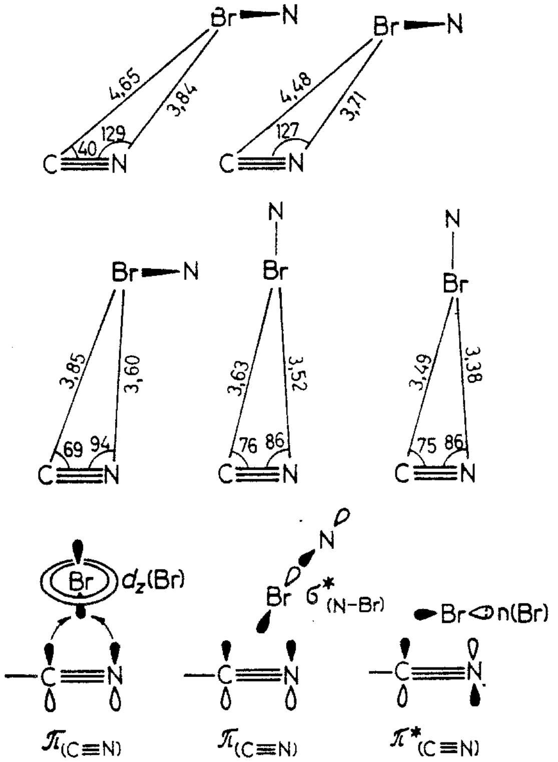
*Communication 16 from the series "Chemistry of 1,1,2,2-tetracyanoethane". See [1] for Communication 15.
†Some of the results were presented in part in [4, 5].

Branch of the Institute of Chemical Physics, Chernogolovka 142432. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 519-526, April, 1991. Original article submitted March 6, 1989.

molecular orbital (LVMO) is localized primarily on the p_π orbital of the C_β atom [6], and, second, the resulting enolate anion is partially stabilized due to p–π^* conjugation in the diacetyl fragment.

It must be noted that the anion conformation presented in the scheme above ensures its additional stabilization due to orbital [(HOMO of the enolate anion)–$\pi^*_{C\equiv N}$] and electrostatic (drawn-together "rigid" [7] $O^{\delta-}$ and $H^{\delta+}$ centers) interactions.* The latter promote transfer of an acidic hydrogen atom to the electronegative oxygen atom and then to the C_α atom to give the diketone, which is thermodynamically more stable than the preceding keto enol. If this transfer is actually realized (which will be demonstrated subsequently), then C–H → O^- attack "from above" (see the scheme) dictates the subsequent 1,3-H shift (from O to C) "from below", since only in this case will the p orbitals of the C and O atoms [the highest occupied molecular orbitals (HOMO)] and the s orbital of the H atom be overlapped in phase (a 1,3-antara-surface shift [7]) during the transfer:



In turn, the approach of the H atom "from above" requires a gauche orientation of the ethyl and acyl groups.† This is followed by aldol condensation with subsequent cyclization and the formation of III. If the latter step is correct, the cyclization should be realized in the cis orientation relative to the ethyl group. According to the results of x-ray diffraction analysis (Fig. 1), the conformation of the III molecule is a "basket" with the acyl group in the exo position and the ethyl group in the endo position, i.e., in a cis orientation relative to the imino ester fragment. Since both of the stereochemical conditions of the proposed pathway are satisfied, the pathway is proved. The result obtained makes it possible to draw the following conclusions.

1. The reaction of tetracyanoethane with diketone V, which contains simultaneously s-trans and s-cis fragments, proceeds via the pathway that is characteristic for systems with an s-cis conformation [3, 4]. It may be assumed that the examined mechanism, which is intramolecular transfer of a proton with subsequent $(NC)_2C^-$...(>C=O) cyclization, is energically more favorable (proceeds faster) than the $C^-(COCH_3)_2$...(–C≡N) cyclization that is characteristic for reactions with the s-trans isomer [2]. This assumption is confirmed qualitatively by the higher donor capacity of the $-C^-(CN)_2$ carbanion as compared with the $-C^-(COCH_3)_2$ anion [the HOMO level of $-C^-(CN)_2$ is higher] and the higher acceptor capacity of the acyl group as compared with the nitrilo group (the LVMO level of C=O is lower).

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*According to data from geometrical modeling, $R_{O...H}$ in the anion ≈2.4 Å.

†One cannot exclude the possibility that intermolecular exchange of the acidic proton between the anion and the solvent with retention of the stereochemistry of the final product of the reaction is realized.

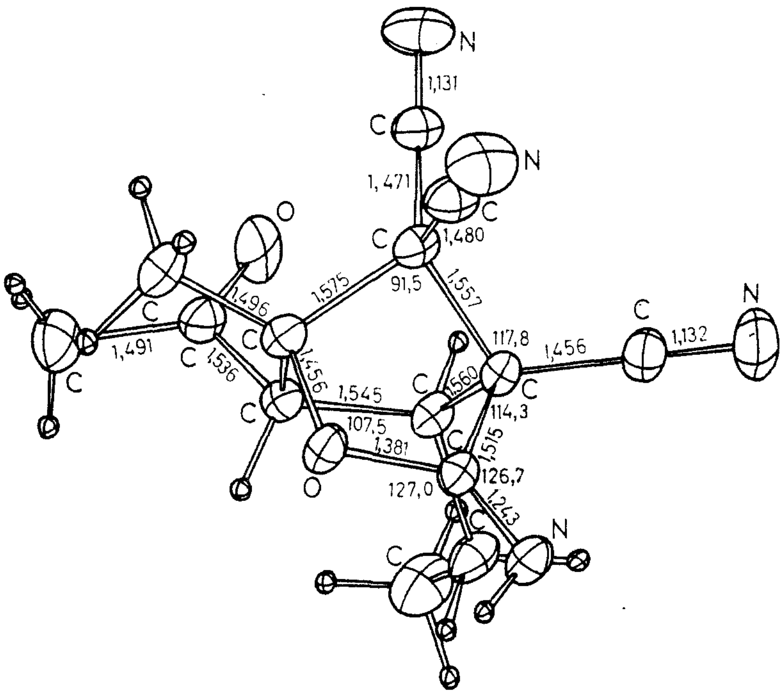


Fig. 1. Structure of the III molecule with 30% probability ellipsoids of the thermal vibrations for the nonhydrogen atoms (the maximum errors in the determination of the bond lengths and bond angles were 0.003 Å and 0.2°, respectively).

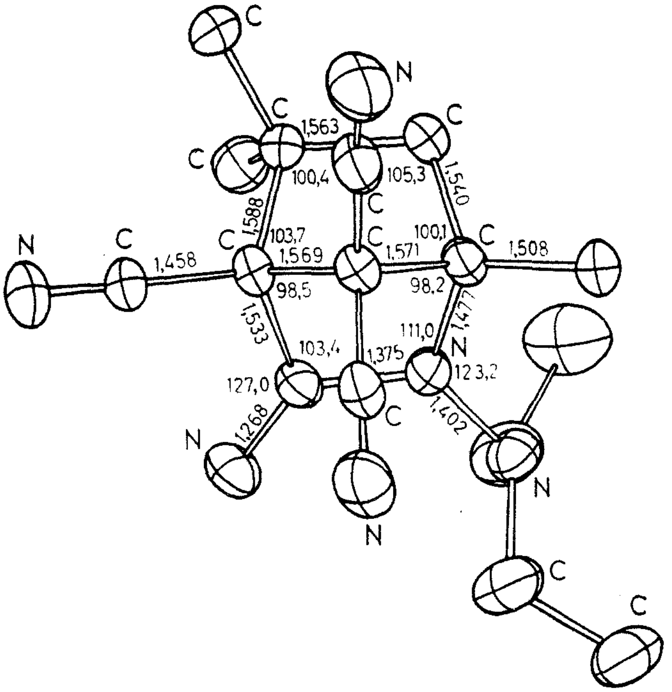
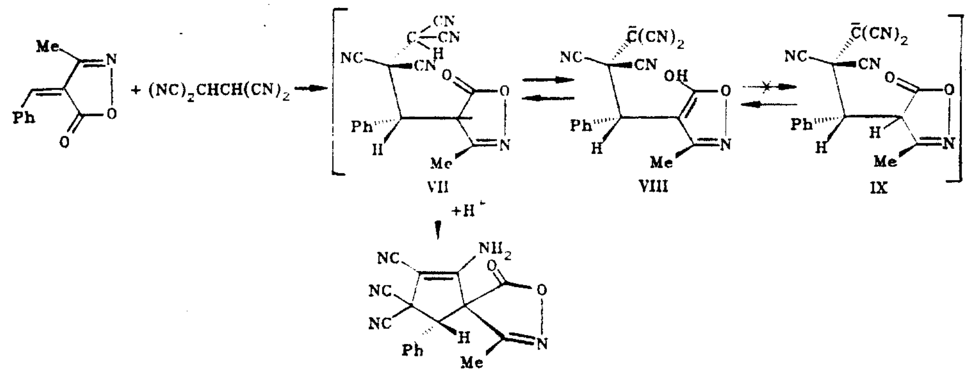


Fig. 2. Structure of the IV molecule with 30% probability ellipsoids of the thermal vibrations (the hydrogen atoms are not presented (the maximum errors in the determination of the bond lengths and bond angles were 0.003 Å and 0.2°, respectively).

2. The reaction of tetracyanoethane with conjugated cyclic systems with exo-s-cis C=C and C=O bonds leads to the formation of spirans [8, 9] rather than bicyclic systems, since, in contrast to the keto enol (compare with the formation of III), intermediate VIII is thermodynamically more stable, inasmuch as a cyclic 6π-electron system is realized. As a consequence of this, a 1,3-shift of a hydrogen atom with the formation and cleavage of a cyclic conjugation chain (VIII → IX) is energically less favorable than the reverse transition (VIII → VII) with retention of

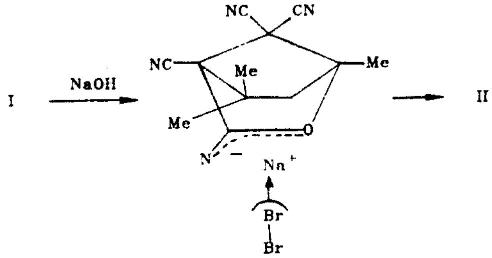
the 6π-conjugated system; subsequent $—C^-(CN)_2 \rightarrow (—C{\equiv}N)$ cyclization leads to the formation of a spiran [9]:

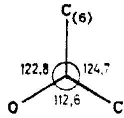


According to the results of x-ray diffraction analysis, a cis orientation of substituent R^4 relative to X is realized in all bicyclic systems.* We assume that the cis conformation is more favorable than the trans conformation, since repulsions of the unshared electron pairs of the O and N atoms are absent, a more effective $n_N—\sigma^*_{C—O}$ interaction is realized [10], and there is considerably less dipole-dipole repulsion of the ester and imine fragments.

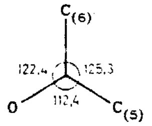
The conclusions are confirmed by the results of nonempirical calculations of the cis and trans isomers of the imino fluoride in the STO-3G basis [11] with complete optimization of the geometry.† The cis isomer is more stable than the trans isomer by 3.0 kcal/mole. The energy level of the HOMO, which is localized primarily on n_N, is −8.6 eV in the cis isomer, as compared with −8.4 eV in the trans isomer. The level of the LVMO, which is localized primarily on $\sigma^*_{C—F}$, is 12.7 eV in the cis isomer, as compared with 12.4 eV in the trans isomer. The calculated dipole moment of the cis isomer is 0.7 D, as compared with 2.3 D for the trans isomer.

Information regarding the structures of I and II makes it possible to observe the stereochemical peculiarities of the bromination of imine I. A salt in which the Na^+ ion is undoubtedly located in the plane of the imino ester anion is formed in the first step. The subsequent bromination automatically leads to a syn orientation of the O and Br atoms in the II molecule.

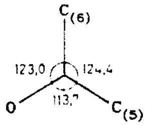




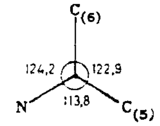
I



II



III



IV

The stereochemistry of the bicyclic carcasses of I-IV is characterized by the $C_{(1)} \rightarrow C_{(3)}$ Newman projection and angles of bending of the "boat" (at the foundation of the bicyclic systems) along the $C_{(2)} \cdots C_{(4)}$ and $C_{(5)} \cdots X$ lines: 65.6° and 62.5° in I, 65.3° and 62.3° in II, 61.5° and 67.0° in III, and 68.0° and 59.0° in IV. The observed tendency for flattening of the "boat" along the $C_{(2)} \cdots C_{(4)}$ lines [and, correspondingly, for an increase in bending of the "boat" along the $X \cdots C_{(5)}$ line] in the order III > I, II > IV is associated with changes in the steric hindrance in the molecules of this series. The intramolecular contacts, which are shortened as compared with the sums of the van der Waals radii of the atoms ($R_{\omega C} \approx 1.7$ Å, $R_{\omega N} \approx 1.5$ Å, $R_{\omega H} \approx 1.17$ Å [12]), constitute evidence for the existence of hindrance. Thus replacement of the hydrogen atom [III, $R_{C_{(8)} \cdots H}$ 2.61(1) Å] by a methyl group [I, II; $R_{C_{(8)} \cdots H(CH_3)}$ 2.45(1) Å] leads to an increase in the steric hindrance, which is compensated in part by the large angle of bending of the "boat"

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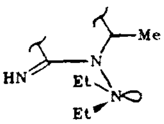
*Two peaks of approximately equal height in the syn and anti orientations with respect to the hydrazino group were detected in the IV molecule in differential synthesis of the electron density in the region of the imine nitrogen atom. We assume that the IV molecule is a cocrystal of the syn and anti isomers.

†A similar analysis of the results of ab initio calculations of $XHC{=}NH$ systems ($X = H, CH_3, NH_2, OH$, and F) will be published later.

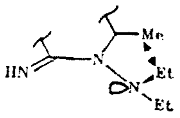
along the $C_{(2)}\cdots C_{(4)}$ line in the I and II molecules. Similarly, bending along the $O\cdots C_{(5)}$ line in the III molecule increases when the hydrogen in the exo-$C_{(5)}$ position [I, II; $R_{C_{(8)}\cdots H}$ 2.75 Å] is replaced by an acyl group [$R_{C_{(8)}\cdots C(O)}$ 3.262(1) Å]. And, finally, the introduction of a bulky diethylamino substituent (IV), as compared with the I and II molecules, ensures steric hindrance of $N(N{=}C)\cdots H(NEt_2)$, which is removed in part [$R_{N\ldots H}$ 2.70(2) Å] due to an increase in bending of the heteroring along the $C_{(2)}\cdots C_{(4)}$ line and flattening of the ring along the $N\cdots C_{(5)}$ line.

It must be noted that the strains caused by the shortest intramolecular contacts — $C_{(8)}\cdots H$(exo-CH_3) 2.45(2) Å, $C_{(8)}\cdots C_{(5)}$ 2.936(2) Å, $C_{(2)}\cdots C$(endo-CH_3) 2.827(2) Å, and $C_{(2)}\cdots H$(endo-CH_3) 2.44(2) Å* — are partially eliminated due to lengthening of the $C_{(3)}{-}C_{(4)}$ [1.585(3) Å], $C_{(3)}{-}C_{(6)}$ [1.564(4) Å], and $C_{(1)}{-}C_{(6)}$ [1.568(3) Å] bonds. An increase in the p character of the orbitals of the $C_{(6)}$ atom due to the $C_{(3)}C_{(6)}C_{(1)}$ angle of 91.3(2)° [13, 14] and specific interactions of the σ_{C-C}, σ^*_{C-C}, $\pi_{C\equiv N}$, and $\pi^*_{C\equiv N}$ orbitals [4] are additional reasons for the lengthening of the bridge bonds. The exocyclic $C_{(3)}{-}C_{(9)}$ [1.457(3) Å], $C_{(1)}{-}C_{(10)}$ [1.498(3) Å], and $C_{(2)}{=}N{-}$ [1.246(3) Å] bonds are shortened by 0.02-0.03 Å as compared with the standard values. This sort of effect is due to the geometry of the [2.2.1]-bicyclic system, for which increased exocyclic bond angles [for $C_{(1)}$ and $C_{(3)}$ $\Sigma_{exo} \approx 346°$, while for $C_{(2)}$ $\Sigma_{exo} \approx 254°$] as compared with the standard values of 328.5° and 240° are characteristic. This sort of increase leads to an increase in the strength of the exo bonds and to their shortening due to an increase in the s character of the orbitals of the carbon atoms [14, 15] and to a decrease in the exo-substituent—bicyclic-system atoms 1,3-repulsions [16]. The significant shortening of the C=N bond in the I and III molecules as compared with the standard value (1.27 Å [17]) explains the anomalously high frequency of the stretching vibrations ($\nu_{C=N} \approx 1725$ cm^{-1}). It should be noted that this short bond is realized under conditions of $n_{p(O)}{-}\pi^*_{C=N}$ conjugation, as evidenced by the planar structure of the imino ester fragment and the shortening of the O—C bond [1.370(3) Å] as compared with the sum of the covalent radii of O (0.66 Å) and C_{sp^2} (0.74 Å). On passing from I and III to II the $n_{p(O)}{-}\pi^*_{C=N}$ conjugation increases due to the electronegativity of the bromine atom;† this is reflected in shortening of the O—C bonds [1.340(3) Å], lengthening of the C=N bonds [1.267(2) Å], and a decrease in $\nu_{C=N}$ to 1670 cm^{-1}. Similarly, stronger $n_N{-}\pi^*_{C=N}$ conjugation,‡ which is reflected in shortening of the N—C bonds [1.378(3) Å], lengthening of the C=N bonds [1.262(2) Å], and a decrease in $\nu_{C=N}$ to 1660 cm^{-1}, is realized on passing from I and III to IV. Let us note that, despite the virtually identical lengths of the O—C (II) and N—C (IV) bonds, the effective shortening (due to conjugation) in the latter is much greater — in the absence of conjugation the length of the $N{-}C_{sp^2}$ bond is 1.45 Å [18].

The unusual Z conformation of the iminohydrazide fragment in IV must be noted.



Z



E

This sort of conformation prohibits the realization of the "apparent" C=NH...N intramolecular hydrogen bond. The results of geometrical modeling show that significant steric hindrance develops between the ethyl and methyl substituents — $R_{H(Me)\ldots H(Et)}$ 1.81 Å — which excludes realization of the hypothetical E structure. The virtually unchanged $C{=}N{-}R^4$ bond angle when a hydrogen atom [I, 114(2)°] is replaced by a bromine atom [II, 117(2)°] is extremely surprising. We suppose that the unchanged value of the angle is associated not only with the slight steric hindrance [the $R_{O\ldots Br}$ value of 2.936(2) Å is 0.3 Å smaller than the sum of the van der Waals radii of the atoms**] but also with specific O...Br stabilizing interactions.

Two polymorphic modifications were detected in the x-ray diffraction analysis of II. In the crystals of each modification the bromine atom has three short intermolecular contacts with the adjacent nitrilo groups, and the distance to the nitrogen atom is always shorter than that to the carbon atom. Two important conclusions follow from this. First, the short contacts with the negatively charged nitrile nitrogen atom constitute evidence that the bromine atom bears a negative charge, i.e., the polarity of the imino bromide is defined as $N^{\delta-}{-}Br^{\delta+}$. Thus a way to determine the polarity of a bond for elements with close electronegativities on the basis of the intermolecular contacts

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*If not specially mentioned, the general principles of the structures of the bicyclic systems are analyzed in the case of the I molecule.

†The bromine atom polarizes the C=N bond, which is reflected in a decrease in the $\pi^*_{C=N}$ level and an increase in the contribution of the AO of the C atom to $\pi^*_{C=N}$ [10].

‡The π-donor capacity of the trivalent nitrogen atom is higher than that of the divalent oxygen atom.

**The length of the O...H bond in the I molecule is 2.47(3) Å.

with atoms with known character is proposed. Second, an analysis of the intermolecular contacts showed that the shortening of the Br···N bond lengths correlates with the decrease in the Br···N≡C—bond angle. Thus the structural data model the electrophilic attack by Br^+ at a triple bond.* Electrostatic interactions dominate at long Br···N distances, and $Br^{\delta+}$ approaches from the rear side of the C≡N dipole. The role of orbital interactions increases near the CN group, and bromine prevails over the cyano group for maximal overlapping of the π orbitals (C≡N) with the σ^*_{N-Br} and d orbitals of bromine, as well as for "back" interactions of the unshared electron pair of bromine with the $\pi^*_{C\equiv N}$ orbitals.

EXPERIMENTAL

The x-ray diffraction study was carried out with DAR-UM (I-III) and RÉD-4 (IV) diffractometers.† The synthesis of I and II was described in [2].

6-Acetyl-1-3-imino-1-methyl-5-ethyl-4,7,7-tricyano-2-oxabicyclo[2.2.1]heptane (III, $C_{14}H_{14}N_4O_2$). A 50-mmole sample of 1,1,2,2-tetracyanoethane was added to a solution of 55 mmole of propylideneacetylacetone [21] in 60 ml of iso-PrOH—H_2O (1:1), and the mixture was heated with stirring to 40-45°C until the tetracyanoethane in the reaction mixture had vanished (6-7 h). The next day the resulting precipitate was removed by filtration and washed with aqueous isopropyl alcohol to give a product with mp 145-146°C in 22% yield.

X-Ray Diffraction Study of III. The principal crystallographic data are as follows: M = 276.3, a = 12.009(3) Å, b = 9.593(3) Å, c = 12.208(3) Å, γ = 87.23(2)°, V = 1404.8(4) $Å^3$, space group $P2_1/n$, d_{calc} = 1.28 g/cm^3, 2208 reflections with $I > 2\sigma(I)$, $\mu_{Cu\ K_\alpha}$ = 7.1 cm^{-1}, R = 0.050.

3-Imino-1,5,5-trimethyl-4,7,7-tricyano-2-ethylamino-2-azabicyclo[2.2.1]heptane (IV, $C_{16}H_{22}N_6$). A 4.3 g (30 mmole) sample of mesityl oxide diethylhydrazone [22] was added to a suspension of 3.9 g (30 mmole) of tetracyanoethane in 30 ml of 2-propanol—water (1:1); the tetracyanoethane dissolved in 5-10 min. The next day imine IV had crystallized out from the reaction mass. It was removed by filtration, washed with aqueous alcohol, and recrystallized from 2-propanol to give 2.4 g (31%) of a product with mp 111-112°C.

X-Ray Diffraction Study of IV. The principal crystallographic data are as follows: M = 298.4, a = 13.052(9) Å, b = 9.670(2) Å, c = 7.261(2) Å, α = 108.80(4)°, β = 99.86(4)°, γ = 87.95(2)°, V = 854.6(2) $Å^3$, Z = 2, space group $P\bar{1}$, d_{calc} = 1.17 g/cm^3, 1872 reflections with $I > 2\sigma(I)$, R = 0.049.

X-Ray Diffraction Study of Imine I. This compound ($C_{12}H_{12}N_4O$) had the following crystallographic data: M = 228.3, a = 6.970(2) Å, b = 7.879(3) Å, c = 11.921(5) Å, γ = 67.10(2)°, V = 603.1(3) $Å^3$, space group $P2_1$, Z = 2, d_{calc} = 1.26 g/cm^3, 1176 reflections with $I > 2\sigma(I)$, $\mu_{Cu\ K_\alpha}$ = 7.0 cm^{-1}, R = 0.028.

X-Ray Diffraction Study of Imine II. The monoclinic modification of this compound ($C_{12}H_{11}N_4OBr$) had the following crystallographic data: M = 270.1, a = 7.189(1) Å, b = 25.415(7) Å, c = 7.228(2) Å, γ = 94.50(3)°, V = 1316.9(6) $Å^3$, Z = 4, space group $P2_1/b$, 2081 reflections, $\mu_{Cu\ K_\alpha}$ = 39.0 cm^{-1}, R = 0.059 (taking absorption into account). The rhombic modification had the following parameters: a = 12.785(5) Å, b = 7.362(3) Å, c = 13.992(5) Å, V = 1316.0(6) $Å^3$, Z = 4, space group $P2_12_12_1$, d_{calc} = 1.37 g/cm^3, 1203 reflections with $I > 2\sigma(I)$, R = 0.044.

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*See a previously published review [19] regarding the mapping of chemical reaction from the results of x-ray diffraction analysis.

†The structures were determined by a direct method by means of the program in [20] and were refined by the method of least squares taking into account the anisotropy for the O, N, and C atoms and the isotropy for the H atoms.

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