below the lines established by the rest of the points. These expected deviations are also consistent with eq i.[3] From the slopes, intercepts, and k_T values for 0.05 M nucleophile concentration, the ratios k_2/k_{-1} are calculated to be the same. Hence the autodecomposition of the intermediate to yield the products or backwards to yield the reactants is an intrinsic property not influenced by the nucleophile concentration or by the attachment of a proton or a deuteron to the nucleophile.

The constancy of k_1 and k_2/k_{-1} values as well as the ratio $k_{B(H)}/k_{B(D)} = 2.1$ suggest that the proposed mechanism is very likely correct. The rate-determining step would be the heterolysis of the N–H bond in the catalyzed pathway. These results suggest that a deuterium isotope effect in aromatic nucleophilic substitutions must be studied using a broad range of nucleophile concentration. Failure in this requirement would explain the reported absence[7,9,12,13] of a kinetic isotope effect in several similar reactions.

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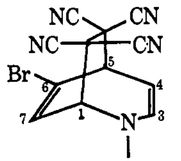
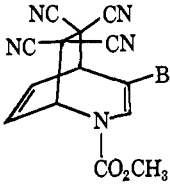
Structure of Cocrystallized Cycloadducts from 3- and 4-Bromo-N-carbomethoxyazepine and Tetracyanoethylene[1,2]

Sir:

The cycloadducts from N-carboxyazepines and tetracyanoethylene have recently been shown[3–5] to result from Diels–Alder reactions, rather than from 2,6 cycloadditions.[6] The monosubstituted azepines derived from monosubstituted benzenes and carbomethoxynitrene gave adducts with tetracyanoethylene identified primarily through nmr spectroscopy as 6-substituted 8,8,9,9-tetracyano-2-carbomethoxy-2-azabicyclo[3.2.2]nona-3,6-dienes[3] (*e.g.*, I). To confirm these assignments and to determine the detailed stereochemical structure of a representative cycloadduct in this class, an X-ray single crystal structure analysis of the solid, thought to be I, was undertaken.



I



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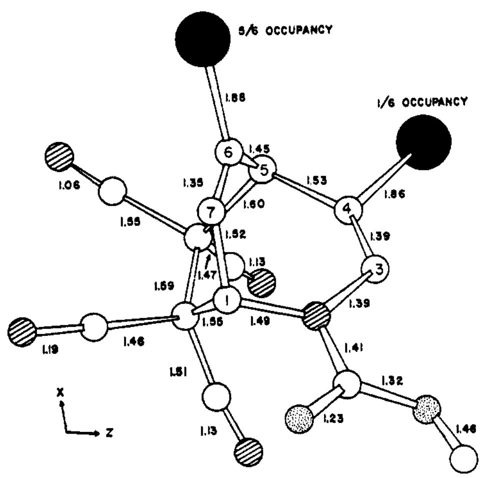

Figure 1. Stereographic view of the cocrystallized molecules I and II along the y axis. The standard deviation of a typical C–C bond is 0.028 A.

The crystals of the adduct (mp 163–167°, recrystallized five times from toluene[7]) belong to the monoclinic system with $a = 19.25 \pm 0.03$, $b = 10.87 \pm 0.02$, $c = 8.98 \pm 0.02$ A, and $\beta = 101° 30' \pm 15'$. The cell parameters were measured from precession photographs (Mo Kα, λ 0.7107 A). The space group is $P2_1/a$ and there are four molecules of $C_{14}H_8O_2N_5Br \cdot 0.5C_7H_8$ in the unit cell; the measured density is 1.49 g/cc compared to the calculated value of 1.46 g/cc. A total of 1605 independent structure amplitudes was recorded visually from equiinclination Weissenberg photographs (Cu Kα, λ 1.5418 A) taken at 3°. The signs of the structure amplitudes were obtained by the heavy-atom method[8] and the molecular structure was shown to be consistent with I. Refinement proceeded to a crystallographic R factor of 0.18, and the calculated distances and angles were in fair agreement with expected values.

It proved impossible, however, to refine the structure beyond this point by least-squares techniques. Furthermore, in the course of the refinement, the temperature factors associated with most of the carbon, nitrogen, and oxygen atoms tended to assume negative values, which correspond to a physically unreal situation. Computation of a difference map at this stage revealed peaks around two of the crystallographic centers of symmetry corresponding to a disordered orientation for the toluene molecules, which had been previously undetected, and an unexpected peak situated approximately 1.9 A from C(4). The density of this peak was close to that expected for a carbon or oxygen atom. With this peak included as a carbon atom in further refinements, the R factor and the sum of the least-squares residuals were successfully reduced. The unexpected peak, however, remained about 1.90 A from C(4) and subtended reasonable bond angles be-

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(1) This work was supported in part by the National Science Foundation (GP-5226) and the National Institutes of Health (GM 12470-02 and 5T1 GM 722-05).

(2) Cycloadditions. VII. Paper VI: J. E. Baldwin and J. P. Nelson, *J. Org. Chem.*, **31**, 336 (1966).

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(7) Analytical data for material prepared by thorough pumping had corresponded to $C_{14}H_8O_2N_5Br$.[3] In the course of the present investigation, an elemental analysis on the crystals being used in the X-ray work indicated the presence of toluene of crystallization, corresponding to $C_{14}H_8O_2N_5Br \cdot 0.5C_7H_8$. Complete removal of toluene afforded material which melted sharply at 167–169°, but which was unsuitable for single crystal studies.

(8) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 219 (1937).

tween C(4) and its neighbors. We have interpreted this peak as a bromine atom in a site which is occupied in approximately one-sixth of the molecules, and conclude that we are dealing here with an example of cocrystallization of isomers I and II in the approximate ratio of 5:1. As the scale factor between the observed and calculated structure amplitudes in a molecule of this size is largely determined by the bromine atom, an overrepresentation of the occupancy of this atom would be expected to result in negative temperature factors for the lighter atoms. Refinement, with the appropriate partial occupancy of the two bromine atoms, has reduced the R factor to 0.144. As the asumption that all the other atoms occupy exactly the same positions in the crystal for the two isomers is probably not quite valid, we feel that this stage of refinement corresponds to the best information that can be obtained about the molecular geometry from an analysis on this crystal.

This study emphasizes several important general points. While a sharply melting organic solid containing some 16% of an isomeric structure is rare, its present detection serves to stress a need for caution in applying the classic criterion for the purity of solids. Furthermore, the possible dangers of accepting information from structural models containing physically unacceptable thermal parameters are clearly indicated, however reasonable the structural results or assuring the R value. It is extremely doubtful if this cocrystallization would have been detected had it not been that the heaviest atom occupied different positions in the two isomers.

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2,6-Diarylpyridines from the Pyrolyses of Phenone Hydrazonium Fluoroborates

Sir:

Potential N–N cleavage reactions of N,N,N-trisubstituted hydrazonium derivatives of carbonyl compounds **1** are either analogous to Hofmann elimination (route a) or should give the incipient cationic intermediate **2** (route b), expected to undergo skeletal rearrangement. Route a has been demonstrated by

$$\mathrm{ACH{=}N{-}\overset{+}{N}R_3\ B^-} \xrightarrow{\mathrm{a}} \mathrm{A{-}C{\equiv}N + R_3N + B{-}H}$$

$$\underset{\mathbf{1}}{\mathrm{ACR'{=}N{-}\overset{+}{N}R_3\ B^-}} \xrightarrow[\mathrm{R'\,=\,alkyl}]{\mathrm{b}} \underset{\mathbf{2}}{\mathrm{ACR'{=}N^+}} + \mathrm{R_3N + B^-}$$

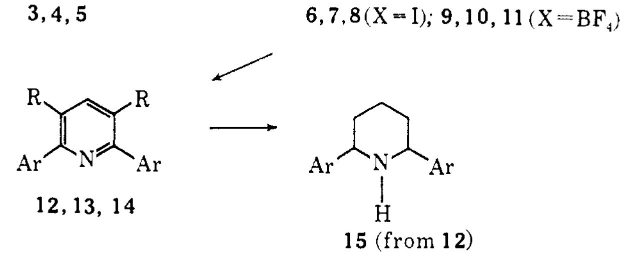
syntheses of nitriles from the base-catalyzed decomposition of aldehyde N,N,N-trimethylhydrazonium iodides or *p*-toluenesulfonates.[1]

The latter potential reaction course, although apparently similar to well-known C–N rearrangements,[2] has been reported not to occur in the pyrolyses of ketone N,N,N-trimethylhydrazonium iodides.[3] Reaction with base under anhydrous conditions, however, gives a variant of the Neber rearrangement.[3,4]

We have pyrolyzed ketone N,N,N-trimethylhydrazonium fluoroborates in an attempt to demonstrate the cationic intermediate **2**. Fluoroborate, as counterion, is less nucleophilic and is a much poorer reducing agent than iodide.

Pyrolysis of anhydrous acetophenone N,N,N-trimethylhydrazonium fluoroborate (**9**), either as a crystalline solid heated to its decomposition point (~200°) or as a suspension in refluxing cumene (~150°), gave 2,6-diphenylpyridine (**12**) and trimethylamine as the major isolable organic products (40–50%). Structural variations of the ketone N,N,N-trimethylhydrazonium fluoroborate gave upon pyrolysis the analogous pyridine derivatives.

Acetophenone N,N-dimethylhydrazone[5] (**3**) with methyl iodide gave acetophenone N,N,N-trimethylhydrazonium iodide[3] (**6**). Treatment of a hot aqueous solution of **6** with aqueous sodium fluoroborate resulted in high yields of acetophenone N,N,N-trimethylhydrazonium fluoroborate (**9**), mp 153–154° dec.



$$\underset{\mathbf{3,4,5}}{\mathrm{ArC(CH_2R){=}N{-}NMe_2}} \longrightarrow \underset{\mathbf{6,7,8}\,(\mathrm{X=I});\ \mathbf{9,10,11}\,(\mathrm{X=BF_4})}{\mathrm{ArC(CH_2R){=}N{-}\overset{+}{N}Me_3X^-}}$$

12, 13, 14

15 (from **12**)

R = CH_3 in **5, 8, 11, 14**, otherwise R = H; Ar = *p*-tolyl in **4, 7, 10, 13**, otherwise Ar = phenyl.

4′-Methylacetophenone N,N,N-trimethylhydrazonium fluoroborate (**10**), mp 159–160° dec, and propiophenone N,N,N-trimethylhydrazonium fluoroborate (**11**), mp 110–111°, dec point ~180°, were prepared in high yields in an analogous manner.

Pyrolysis of **9**, **10**, or **11** at ~200°, either under a slow stream of nitrogen or *in vacuo*, afforded a tarry residue, which was extracted, then purified by elution chromatography on neutral alumina with petroleum ether. **9** gave 2,6-diphenylpyridine (**12**), mp 82–83° (lit.[6] mp 82°), **10** yielded 2,6-di-*p*-tolylpyridine (**13**), mp 165–165.5° (lit.[7] mp 162°), and **11** afforded 2,6-diphenyl-3,5-dimethylpyridine (**14**), mp 136–137° (lit.[8] 134–135°); nmr (CCl_4) displayed a doublet at τ 2.74 (C_{aromatic}–CH_3) with a coupling constant of J = 0.5 cps and a multiplet at τ 2.6 (aromatic protons) with relative intensities 6:11, respectively; mol wt, 259 (mass spectroscopy).

Reduction of **12** with sodium and ethanol gave 2,6-diphenylpiperidine (**15**), characterized as its picrate, mp 204° (lit.[9] mp 198°).

The elemental analyses and spectral data of all the compounds agree with the assigned structures.

Isolation of **14** from pyrolysis of **11**, in which the methyl groups are at positions 3 and 5 of the pyridine

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