ference into volumetric flasks and diluted with absolute ethanol. Rate constants were determined for the disappearance of the nitrone by following the decrease in its absorption at 293.5 (for **3**) and 310 nm (for **5**).

Product Analyses. Small samples of **5** were decomposed (99.9% reaction based upon rates) in *tert*-butyl alcohol at 144°. After removal of solvent under reduced pressure, the residue was carefully chromatographed over alumina. Hexane-benzene (49:1) mixtures eluted approximately 1-2% tetraphenylethane. Hexane–benzene (4:1) eluted *O*-benzhydrylbenzophenone oxime in yields as high as 96%.

The yield of benzaldoxime from the decomposition of **3** in *tert*-butyl alcohol (measured by ultraviolet spectroscopy) was 97%. The opened reaction ampoules were then attached to a vacuum line, and the isobutylene was distilled from the solution and collected under reduced pressure. The isobutylene (90% determined volumetrically) was identified by infrared and mass spectra.

Acknowledgment. The authors wish to thank Dr. Morey Ring for his assistance in isolating the isobutylene using vacuum line techniques.

Registry No.—**1,** 7731-34-2; **3,** 52392-70-8; **5,** 5350-59-4; *N*-benzyl-*tert*-butylimine, 6852-58-0.

References and Notes

(1) This work was supported in part by the National Science Foundation in a grant (GY-9550) to M.H.G. for an Academic Year Extension of Research Participation for College Teachers.

(2) The rate data for the thermal decomposition of *N*-benzhydryl-α,α-diphenylnitrone (also described in this note) were taken from the Ph.D. thesis of J. A. Villarreal. This part of the study was supported by the National Cancer Institute, National Institutes of Health, U. S. Public Health Service (Grant No. CA-10741-04).

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Thermolysis of Heterocyclic Azides. Rearrangement Involving Acyl Migration from Carbon to Nitrogen

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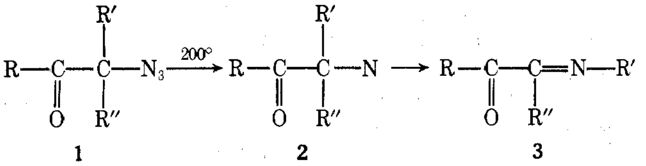
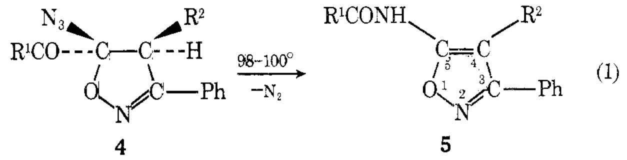
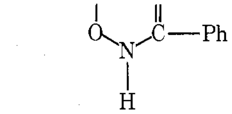
Boyer and Straw have shown that aliphatic α-azidocarbonyl compounds (**1**) decompose at 200 ± 20° to give imines (**3**), probably *via* the intermediacy of nitrenes (**2**).[1] In this reaction migration of hydrogen, methyl, or phenyl occurred and no acyl migration was observed. We now want to report two examples of acyl migration from carbon to nitrogen when R′ and R″ are part of a heterocyclic ring such as in eq 1.[2]





a, R^1 = Me; R^2 = Ph
b, R^1 = Ph; R^2 = Me

The 5-azido-5-acylisoxazolines **4a** and **4b** used in this work were obtained, among other products, from the reactions of α-azidovinyl ketones with benzonitrile oxide.[3] Thermolysis of **4a,b** in toluene at *ca.* 100° resulted in evolution of nitrogen and formation of white crystals which exhibited microanalyses and spectral data consistent with structure **5a,b.** The alternative structures **6** and **7,** which would result from **4** by loss of nitrogen and ring expansion, are easily excluded by the absence of a ketone C-atom absorption at about 190–200 ppm in the ^{13}C nmr spectra.



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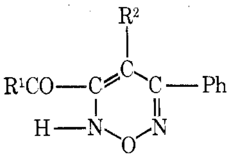

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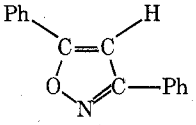
The chemical shift data of compounds **4a** and **4b** are summarized in Table I. Assignment of the ring carbon absorptions was based on comparison with the model compounds **8** and **9.**[3] These compounds possess CH ring C atoms whose position in the nmr spectra can be determined by the off-resonance spin-decoupling technique. The values reported in Table I are consistent with expectation. Indeed,

Table I
^{13}C Chemical Shifts with Respect to TMS (DMSO-d_6 as Solvent)

Compd	C_3	C_4	C_5
5a[a]	162.4	110	159.1
5b[b]	163.6	103.8	159.5
8	164	97.5	170.5
9	161.6	119.3	163.6
11	161.7	91.4	167.7

[a] For this compound the CH_3CO carbon atoms absorb at δ 22.6 and 170. Compare these values with δ 24.1 and 169.5 for the acetyl group in acetanilide: L. F. Johnson and W. C. Jankowski, "Carbon-13 Nmr Spectra. A Collection of Assigned, Coded, and Indexed Spectra," Wiley-Interscience, New York, N.Y., 1972, Spectrum no. 295. [b] For this compound the CH_3 and C=O carbon atoms absorb at δ 8 and 165.6.



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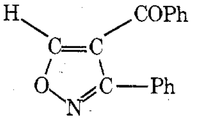

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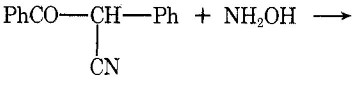
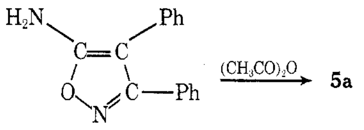
the C_5 atoms are expected to absorb at low field (relative to benzene, δ 128) since they are located next to an electronegative O atom. The C_4 atoms, on the contrary, experience an electron-donating resonance effect of the O atom and, hence, their absorption lines are shifted upfield.

The structure **5a** was further proven beyond any doubt by an independent synthesis starting from α-benzoylphenylacetonitrile (**10**) and hydroxylamine.[4] The aminoisoxazole **11** formed in this reaction was treated with acetic anhydride at room temperature to give a product which was identical in all respects with the product obtained by thermolysis of **4a**. The aminoisoxazole **11** was also subjected to ^{13}C nmr analysis and exhibited absorptions consistent with its structure (see Table I). Noteworthy is the lower field absorption of the C_5 atom compared with the corresponding acetyl derivative **5a**. The difference in chemical shift (8.6 ppm) is comparable with that found for the C_1 absorptions of aniline (δ 147.9) and acetanilide (δ 139.8, $\Delta\delta$ 8.1 ppm).[5] Note also that the C_4 atom in **11** not only experiences the mesomeric effect of the O atom, but also that of the amine function which results in a high-field absorption.



$$\mathrm{PhCO{-}\underset{CN}{CH}{-}Ph + NH_2OH \longrightarrow}$$

10



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Mechanistically, three pathways can be considered for the reaction **4** → **5** (see Scheme I). The azidoisoxazoline **4** can lose nitrogen to give a nitrene **12**, which then rearranges *via* a nitrenium ion **13** as shown in path a, or the azide can decompose with simultaneous formation of the nitrenium ion **13** as shown in path b. A third possible route involves the elimination of HN_3 at the elevated temperature to produce an 5-acylisoxazole **14** which then undergoes a Schmidt reaction to give **5** (path c). Path c is easily excluded by two facts: (i) 5-acylisoxazoles do not react with HN_3 in boiling toluene, and (ii) reaction under the Schmidt conditions (concentrated sulfuric acid) does not lead to **5** but, instead, is known[6] to produce amides of type **15**. We have prepared compound **15a** from **14a** by the well-known Schmidt reaction[7] in order to compare its spectral characteristics with those of compound **5a** (see Experimental Section). Worth mentioning are the ^1H nmr spectra of both compounds, which showed CH_3-NH coupling in the case of **15a** but not in the case of **5a**, the latter giving rise to a Me singlet absorption and a sharp NH absorption.

Scheme I

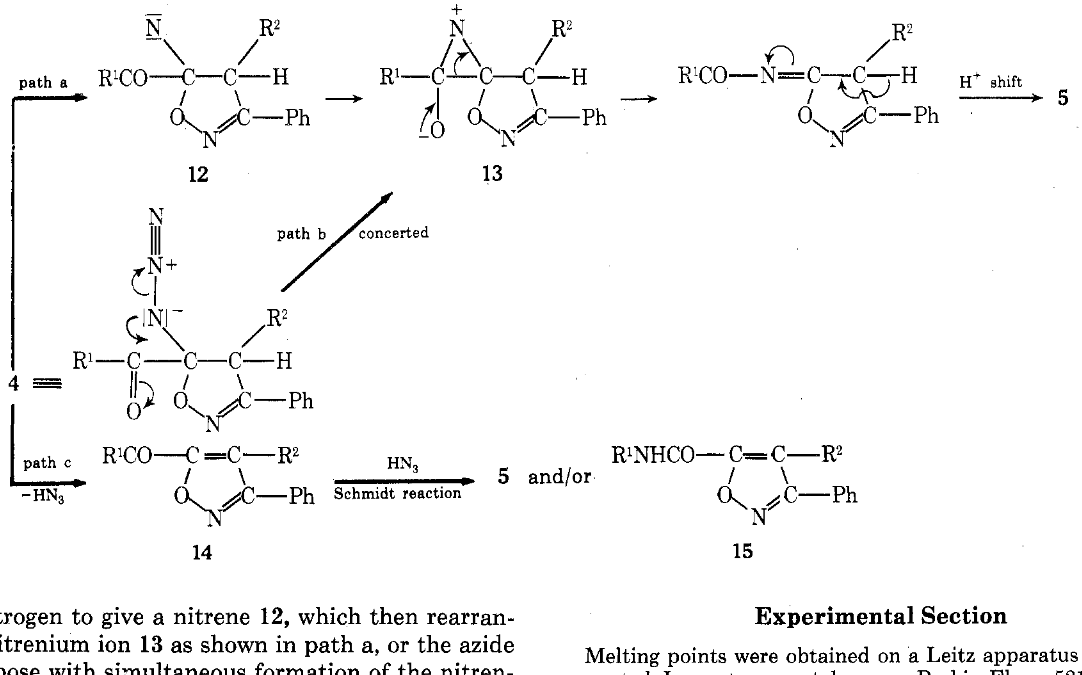

Table II
Rate Constants and Activation Parameters for the Thermal Decomposition of 4a in Decalin

Temp, °C	$10^5 k_1$, sec^{-1}	E_a, kcal/mol	ΔS^* (at 101.9°), eu
101.9	4.76	27.9	−6
110.9	11.61		
121.3	31.94		
131.6	74.19		

Since path c can be excluded on the basis of structure determination, we are left with paths a and b, which only differ in the way the nitrenium ion is formed. In order to differentiate between a two-step or concerted process, we have carried out a kinetic investigation of the thermolysis of **4a** in decalin. The results are summarized in Table II. The moderate energy of activation and the low entropy of activation are only consistent with path b (compare these values with E_a = 47.5 kcal/mol and ΔS^* = +32 eu for thermolysis of cyclohexyl azide in ethyl acetate, which proceeds *via* a nitrene).[8] That anchimeric assistence occurs during the thermolysis of **4a** is also evident from the low decomposition temperature (*ca.* 100°) compared with that of aliphatic α-azidocarbonyl compares (*ca.* 200°).[1]

Experimental Section

Melting points were obtained on a Leitz apparatus and are uncorrected. Ir spectra were taken on a Perkin-Elmer 521 spectrometer. ^1H nmr spectra were recorded with a Varian A-60 or XL-100 spectrometer using TMS as an internal reference. For ^{13}C nmr spectra, the XL-100 apparatus was equipped with a device for pulsed Fourier transform operation. Mass spectra were obtained with an AEI MS-12 instrument operating at an ionizing potential of 70 eV.

Thermolysis of 4a. Compound 4a (1.7 g) was dissolved in dry toluene (10 ml) and then heated at 98–100°. After complete reaction (11 days), the solution was cooled and 5a crystallized out in

72% yield: mp 154–157° ($CHCl_3$-n-pentane); ir (KBr) 3240 (NH), 1692, 1640, 1515 cm^{-1}; nmr ($CDCl_3$) τ 1.68 (NH, exchangeable with D_2O), 2.5–2.8 (m, 10 H), and 7.90 (s, 3 H); mass spectrum m/e (per cent) 278 (60, $M^{\cdot +}$), 236 (100, $M^{\cdot +} - CH_2CO$, m* at m/e 200.3), 235 (11, $M^{\cdot +} - CH_3CO^{\cdot}$).

Anal. Calcd for $C_{17}H_{14}N_2O_2$ (278): C, 73.37; H, 5.07; N, 10.07. Found: C, 73.65; H, 5.08; N, 9.93.

Thermolysis of 4b. When a toluene solution of **4b** (1.0 g in 5 ml) was heated at 98–100° and then cooled, compound **5b** was obtained in 98% yield: mp 148–149.5° (1:1 $CHCl_3$–ether); ir (KBr) 3270 (NH), 1680, 1642, 1530 cm^{-1}; nmr ($CDCl_3$) τ 1.00 (NH, exchangeable with D_2O), 1.8-2.2 (m, 2 H), 2.25–2.75 (m, 8 H), and 7.98 (s, 3 H); mass spectrum m/e (per cent) 278 (54, $M^{\cdot +}$), 175 (16, $M^{\cdot +} - PhCN$), 105 (100, $PhCO^+$).

Anal. Calcd for $C_{17}H_{14}N_2O_2$ (278): C, 73.37; H, 5.07; N, 10.07. Found: C, 73.06; H, 5.08; N, 10.00.

Independent Synthesis of 5a. α-Benzoyl phenylacetonitrile (**10**, 0.02 mol), prepared by the method of Levine and Hauser,[9] was dissolved in pyridine (7 ml) and treated with $NH_2OH \cdot HCl$ (0.02 mol) at room temperature for 24 hr. The suspension was poured into ice–water, and the precipitate was filtered, washed with water, and dried over P_2O_5 to give **11** in 56% yield. Crystallization from water–EtOH (60%) furnished white needles: mp 152–154°; ir (KBr) 3400 (NH), 3300–3180, 1634 cm^{-1}; nmr ($CDCl_3$) τ 2.50–2.90 (m, 10 H) and 5.47 (NH_2, exchangeable with D_2O); mass spectrum m/e (per cent) 236 (41, $M^{\cdot +}$), 208 (27, $M^{\cdot +} - CO$, m* at m/e 183.3), 105 (100, $PhCO^+$).

Anal. (determined by high-resolution exact mass measurement). Calcd for $C_{15}H_{12}N_2O$: 236.09495. Found: 236.09391.

Another procedure for the preparation of **11** consisted in allowing equimolar amounts (0.04 mol) of **10** and $NH_2OH \cdot HCl$ in EtOH (75 ml) to react at reflux temperature for 2 hr. Then the solution was partially evaporated and cooled to give **11** in 58% yield.

Compound **11** (1.2 g) was dissolved in acetic anhydride (15 ml) and allowed to stand at room temperature for 28 days. After cooling of the reaction mixture, **5a** crystallized out in 70% yield, mp 154–157° (benzene).

Note: When **11** was heated in acetic anhydride or in boiling m-xylene containing acetyl chloride, the N,N-diacetylated derivative (mp 145–146.5°) was obtained in high yield (67–84%).

Synthesis of 15a by the Schmidt Reaction. To a magnetically stirred solution of **14a** (0.5 g) in chloroform (15 ml) was added slowly concentrated sulfuric acid (15 ml) and then NaN_3 (1 g). The mixture was stirred for 24 hr at room temperature before being quenched into ice. The yellow precipitate was filtered and crystallized from MeOH (20 ml) to give pure **15a** in 61% yield: mp 196–198°; ir (KBr) 3320 (NH), 1662, 1628, 1530 cm^{-1}; nmr ($CDCl_3$) τ 2.75 (s, 10 H), 3.32 (br, NH, exchangeable with D_2O), and 7.20 (d, 3 H, J = 5 Hz); mass spectrum m/e (per cent) 278 (35, $M^{\cdot +}$), 220 (100, $M^{\cdot +} - CH_3NHCO\cdot$, m* at m/e 174.1), 192 (30, 220 − CO, m* at m/e 167.5).

Anal. Calcd for $C_{17}H_{14}N_2O_2$ (278): C, 73.37; H, 5.03; N, 10.07. Found: C, 73.40; H, 5.05; N, 10.00.

Kinetic Measurements. Decalin solutions of **4a** (*ca.* 1.25 g in 50 ml) were allowed to decompose at the appropriate temperature and the rates of decomposition were followed by recording the decrease of the azide absorption band at about 2130 cm^{-1} in the ir as a function of time. Details concerning the procedure have been described elsewhere.[10]

Acknowledgment. The authors are indebted to the IWONL (Belgium) for a fellowship to one of them (G.M.).

Registry No.—**4a,** 51002-99-4; **4b,** 51003-00-0; **5a,** 52392-71-9; **5b,** 52392-72-0; **10,** 5415-07-6; **11,** 52392-73-1; **11** N,N-diacetylated derivative, 52470-18-5; **14a,** 1631-96-5; **15a,** 52438-82-1; $NH_2OH \cdot HCl$, 5470-11-1.

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Convenient Synthesis of the Tricarbonyliron Complex of Cyclobutadienecarboxylic Acid[1]

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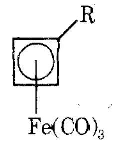
Received June 5, 1974

Recently, in connection with another synthetic program, we needed a convenient source of synthetically useful amounts of the tricarbonyliron complex of cyclobutadienecarboxylic acid (**1b**). Earlier preparations of this compound require parent complex **1a** and involve either formylation–oxidation in <1% overall yield[2] or methylthioformylation–hydrolysis in 34% yield.[2b] Because existent methods for preparing **1a** are either expensive or inefficient, we sought a more direct route to **1b** and have found that application of the photopyrone route of Rosenblum and Gatsonis[3] to the readily prepared 3-carbomethoxy-2-pyrone (**2**)[4] provides a convenient entry to monocarboxyl derivatives of **1a** and, by implication, to other types of monosubstituted derivatives.

Experimentally, a solution of **2** in THF is irradiated until disappearance of the pyrone, and the presumed photopyrone **3** is irradiated for 1 hr in the presence of a 100% excess of iron pentacarbonyl. Although the immediate product, methyl ester **1c**, is isolable, it is a liquid and is sensitive to light. Consequently, the product was most conveniently isolated as crystalline **1b** after a saponification step. Qualitative analysis of the effect of varying irradiation time (during complexation) and relative amount of iron pentacarbonyl indicated that the maximum yield (21%) of **1b** is obtained under the specified conditions.



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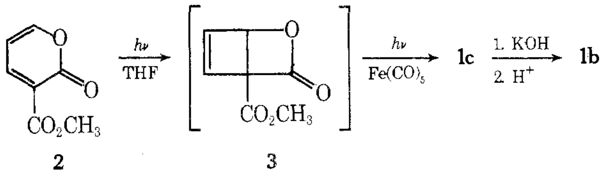

2 3

a, R = H
b, R = CO_2H
c, R = CO_2CH_3

Experimental Section

Melting points and boiling points are uncorrected. Ir spectra were recorded on a Perkin-Elmer 521 spectrophotometer. Nmr spectra were recorded on a Varian Associates A60-A spectrophotometer using TMS as internal standard. Microanalysis was performed by Galbraith Laboratories, Knoxville, Tenn.

Tricarbonyl[1,2,3,4-η-1,3-cyclobutadienecarboxylic acid]iron (1b). A solution of 1.00 g (6.50 mmol) of 3-carbomethoxy-2-