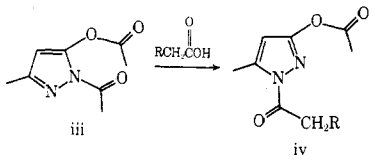
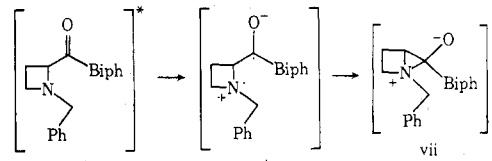
(16) This type of mechanism was demonstrated by labeling experiments for the interconversion of *O*- and *N*-acyl isomers in another heterocycle system: A. W. K. Chan and W. D. Crow, *Aust. J. Chem.*, 2967 (1968).
(17) A similar mechanism was set forth for the conversion of iii to iv: K. Arakawa, T. Miyasaka, and H. Ochi, *Chem. Pharm. Bull.*, 214 (1974).



iii iv

(18) *N*-Acylaminoazetidin-2-ones have been previously reported; see E. Testa and L. Fontanella, *Farmaco, Ed. Sci.*, 1017 (1971).
(19) A similar mechanism involving a bicyclo[2.1.0] intermediate, vii, has been proposed in the photolysis of compound v: A. Padwa, F. Albrecht, P. Singh, and E. Vega, *J. Am. Chem. Soc.*, **93**, 2928 (1971).



v* vi vii

(20) Another process which might compete with β-lactam formation is radical cleavage of the relatively weak N–N linkage. Although this mode of reaction has been observed for monoacylhydrazides,[21] 1,1-diacylhydrazides (**5** is a 1,1-diacylhydrazide) have been shown not to undergo this type of reaction.[21]
(21) R. S. Davidson and A. Lewis, *Tetrahedron Lett.*, 4679 (1973).
(22) Product **11** from the photolysis of **5e** in methanol probably occurred by a similar type II mechanism.
(23) A similar 1-aminoazetidin-2-one has been synthesized thermally. See F. D. Greene, R. L. Camp, V. P. Abegg, and G. O. Pierson, *Tetrahedron Lett.*, 4091 (1973).

On the Generation and Reactivity of *N*-Pyrazolyl Radicals in Benzene Solution[1]

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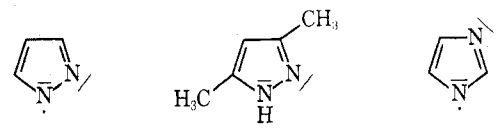
The synthesis of *tert*-butyl 1-pyrazolepercarboxylate (**5a**) and of its 3-methyl derivative **5b** is described. Thermolysis of these compounds in benzene solution at ~140° proceeds predominantly via homolysis and leads to N-phenylated pyrazoles without formation of isomeric *C*-phenyl derivatives. *N*-Pyrazolyl radicals, which are proposed as intermediates, apparently are able to effect homolytic aromatic substitution. Judging from competition with *p*-dichlorobenzene (partial rate factor ~0.25), 1-pyrazolyl (**1**) has a marked electrophilic character. Photolysis of *N*-nitropyrazoles in benzene solution, also leading to N-phenylated derivatives, constitutes an alternative fashion for the generation of *N*-pyrazolyl radicals. Using 3- and 5-substituted pyrazoles as precursors, it is shown that the unpaired electron is delocalized over (at least) the two nitrogen atoms. A σ-type ground state is favored over a π-type electronic structure.

Pyrazolyl radicals—and in general radicals derived from aromatic heterocyclic compounds containing a pyrrole-like nitrogen—can be divided in two classes, viz. (i) radicals which result from homolytic cleavage of a group bound to carbon, and (ii) those formed by such a removal of a substituent on nitrogen. The type i radicals are expected to be closely analogous to homocyclic aryl radicals like phenyl, having the unpaired electron localized in a σ-type orbital.[2] A type ii radical can a priori be compared with both aryl and amino radicals, the latter normally having a π-type electronic ground state.[3]

As an outgrowth of our study on the mechanism of the thermal rearrangement of *N*-nitropyrazoles (resulting in the isomeric 3(5)-nitropyrazoles),[4] we wished to learn about the physical and chemical properties of 1-pyrazolyl (**1**) (Chart I) and its derivatives. To the best of our knowledge **1** is as yet unknown.[5] Recently, Taguchi et al.[6] generated the 4-pyrazolyl radical **2** via decomposition of the parent 4-diazopyrazole in benzene. As anticipated, this type i radical led to the formation of the corresponding 4-phenylpyrazole. A 3,5-diphenyl-1-pyrazolyl radical, thus of type ii, was postulated by Lempert,[7] but there the phenyl rings might strongly influence the character of the radical, as in the well-known polyphenyl substituted pyrryl[8] and imidazolyl[9] radicals.

As regards the electronic ground state of **1**, interaction of the σ orbitals on the two nitrogen atoms has to be considered. Assuming that **1** has C_{2v} symmetry, it may have its unpaired electron in a σ-type orbital, arising from the combination of two N–σ orbitals ($^2B_2$ state); alternatively, the unpaired electron may reside in a π-type orbital involving all five ring atoms ($^2A_2$ or $^2B_1$ state). No information exists about the actual electronic ground state of **1**. For the related 1-imidazolyl (**3**), Evleth et al.[10] predict a $^2B_2$ (σ) ground state, whereas the ESR data of Samuni and Neta[11] strongly point to a π-type electronic structure.

Chart I



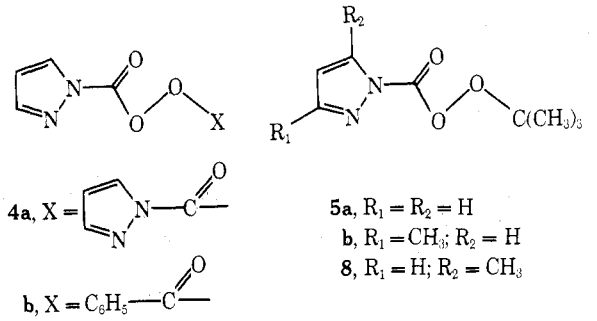
1 2 3

In order to shed light on this matter from a theoretical viewpoint, a series of ab initio SCF calculations is now being performed by Mulder et al. (from the Department of Theoretical Organic Chemistry of our laboratory).[12]

The present paper deals with the generation and reactions of **1** and its 3(5)-methylated analog(s). Several attempts to synthesize the peroxides **4a** and **4b** (Chart II) as precursors for **1** were unsuccessful.[13] The preparation of the *tert*-butyl perester **5a** and of its 3-methyl analog **5b** offered no difficulties, however. Here we report on the thermal decomposition of these novel peresters in benzene solution.

Photolytic decomposition of *N*-nitropyrazoles in benzene has also been considered as a source of **1** and derivatives;

Chart II

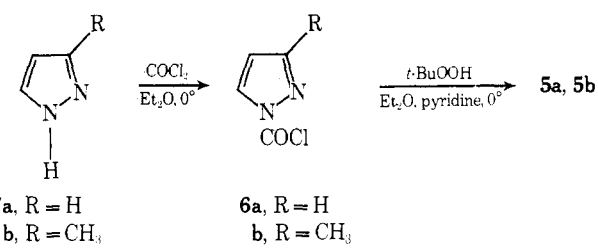


the results are compared with those of the perester decomposition. Finally, the character of the intermediate *N*-pyrazolyl radicals is discussed.

Results and Discussion

The *tert*-butyl perester **5a** and its 3-methyl analog **5b** were prepared via the 1-pyrazolecarbonyl chlorides **6a** and **6b** (Scheme I). The preparation of **6b** by the reaction of 3(5)-methylpyrazole (**7b**) has been described by von Auwers;[15] **6a** was synthesized analogously. The peresters were purified by distillation under reduced pressure and were characterized by their ir and NMR spectra. Compound **5b** appeared to be contaminated with ~4% of its 5-methyl isomer **8**, probably originating from the corresponding acid chloride which may be formed—in addition to **6b**—from **7b**.

Scheme I



Thermolyses of **5a** were performed in sealed tubes, or in an autoclave under nitrogen atmosphere. Typically, a 10% solution of **5a** in benzene was heated in a sealed tube for 1 hr at 135°. As for the fate of the *tert*-butoxy group, NMR spectroscopy showed the formation of *tert*-butyl alcohol, acetone, and toluene, proving the intermediate production of *tert*-butoxy radicals. In addition, isopropenyl methyl ether was found, indicating the occurrence of a competing Criegee-type rearrangement[16] (Scheme II).

Table I
Products from Thermal Decomposition of 5a in Benzene at 135°

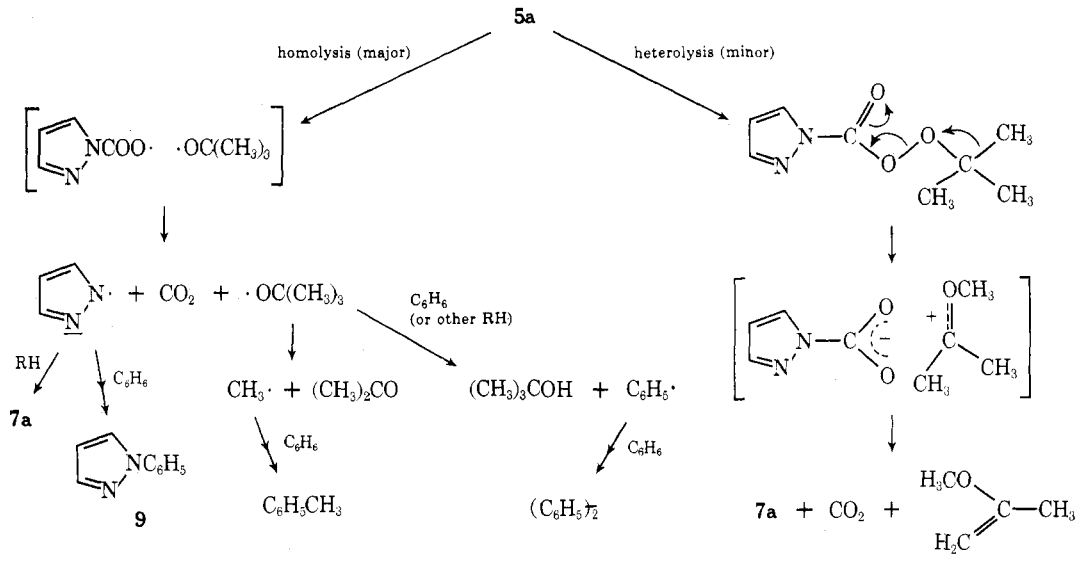
Product	Yield[a] 1 wt % soln	Yield[a] 10 wt % soln
Pyrazole[b]	69	75
1-Phenylpyrazole[b]	17.5	6
(Pyrazolyl group recovery[c]	86.5	81)
tert-Butyl alcohol[d]	*e*	9
Acetone[d]	*e*	51
Isopropenyl methyl ether[d]	*e*	21
(*tert*-Butoxyl group recovery	*e*	81)
Biphenyl[b]	8.5	2
Toluene[d]	*e*	13

[a] In mole percent on basis of the amount of starting material. [b] Fraction isolated from column chromatography (see text). [c] A number of incompletely separated, unidentified products (mostly pyrazole derivatives) was also obtained. [d] By nmr analysis. [e] Not determined.

Column chromatography was used to isolate derivatives formed from the *pyrazolyl* residue, and other higher boiling products. With the aid of NMR and mass spectroscopy, the formation of pyrazole (**7a**), 1-phenylpyrazole (**9**), and biphenyl was demonstrated, yields being dependent on the perester/benzene intake ratio (Table I). The occurrence of peaks from C_{13} and C_{14} hydrocarbons in the mass spectrum of the biphenyl fraction, and of NMR signals in the 1–3 and 5–6-ppm regions, suggest the presence of methylated and hydrogenated biphenyls in the fraction. Likewise, the pyrazole fraction appeared to contain a few percent of 3(5)-methylpyrazole (**7b**), while the *N*-phenylpyrazole fraction most probably contained 1-cyclohexadienylpyrazole. *No C-phenylated pyrazoles could be detected.*

These observations strongly point to a regular homolytic decomposition of perester **5a** as the major pathway, leading to pyrazolyl radical **1**. *tert*-Butoxy radicals are capable of abstracting H atoms from benzene, giving *tert*-butyl alcohol and phenyl radicals,[17] the latter species leading to bi-

Scheme II



phenyl. At the temperatures used, *tert*-butoxy radicals will decompose partly, the methyl radicals being responsible for the production of toluene via homolytic alkylation of benzene; the other arenes present may be methylated analogously. Pyrazole may be produced *via* both radical and nonradical pathways (cf. Scheme II).

1-Phenylpyrazole (**9**) is thought to be formed via **1** by a normal homolytic substitution reaction involving benzene. An alternative pathway for the formation of **9** could perhaps be homolytic phenylation of pyrazole, *selectively on nitrogen.* As far as we know, homolytic phenylation of *unsubstituted* pyrazole has not yet been investigated. We found that when dibenzoyl peroxide (2 mol %) was thermolyzed at 135° in a 1:10 (molar) mixture of pyrazole and benzene, phenylation of pyrazole mainly took place at the 3(5) position, with a partial rate factor (f) of ~1.5 relative to a position in benzene.[18] The amount of 1-phenylpyrazole corresponds to $f \leq 0.6$, substitution at C-4—if any—having $f < 0.2$. Comparing these results with those of thermal decomposition of **5a** in benzene, leading to only N-phenylated pyrazole, we can exclude the alternative of phenylation of pyrazole as an important pathway in the formation of **9** from **5a.**

On the basis of the rate of decomposition of **5a** (suggesting a half-life of the order of magnitude of 0.1 hr at 135°) one-bond O–O homolysis is not unlikely. Thus, another mechanism for the formation of **9** may obtain, viz. formation of phenyl ester **11** from benzene and intermediately formed *N*-pyrazolecarboxyl radicals, followed by (rather rapid) decarboxylation to give **9.**[19] However, this pathway could be excluded, as independently prepared **11** was found to be stable under the experimental conditions for perester thermolysis.

Information as regards the *polar character* of **1** was obtained through the thermal decomposition of **5a** in a mixture of benzene and *p*-dichlorobenzene.[20] From the product ratio 1-(2,5-dichlorophenyl)pyrazole/1-phenylpyrazole (**9**), the partial rate factor for a position in *p*-dichlorobenzene was calculated to be ~0.25.

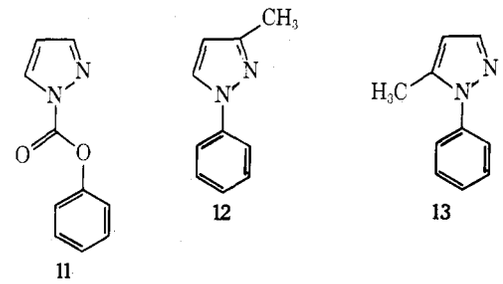
Unfortunately, NMR analysis during decomposition of **5a** in C_6D_6 or in hexachloroacetone at 140° did not reveal any CIDNP effects.

More insight into the electronic structure of *N*-pyrazolyl radicals can be obtained when studying asymmetrically substituted analogs of **1.** If **1** has a σ-type ground state, it either has its unpaired electron localized on N-1, or—more likely—has equal spin densities on N-1 and N-2; for a π-type structure the latter situation also holds. Introduction of asymmetry (by a substituent in the 3 or 5 position) may result in unequal spin densities on both nitrogens in the case of delocalization.

In the first case (localization on N-1), thermolysis of a 3-substituted perester in benzene would result in the 3-substituted 1-phenylpyrazole only; analogously, a 5-substituted derivative would give the isomeric 5-substituted 1-phenylpyrazole. In the second case, that of delocalization, both substrates would give the same result, a mixture of 3 and 5 derivatives in the same ratio.

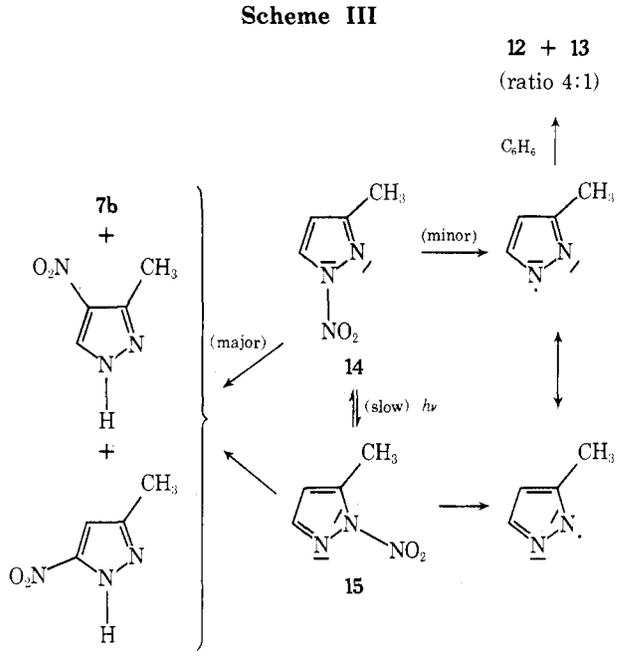
When a 2% solution of the 3-methyl substituted perester **5b** in benzene was heated for 1 hr at 150°, the products isolated by column chromatography were 3(5)-methylpyrazole (**7b,** 80%), biphenyl (~4%), and both 3-methyl-1-phenylpyrazole (**12**) (Chart III) and 5-methyl-1-phenylpyrazole (**13**), ~10%, in a 4:1 ratio. Essentially the same isomer ratio was found by GLPC analysis of the crude reaction product from thermolysis of **5b** in benzene; moreover, *no C-phenylated pyrazoles could be detected in this fashion.* A control run showed that no mutual isomerization of the *N*-phenylpyrazoles **12** and **13** took place under the experimental conditions of thermolysis.

Chart III



In itself, this result on **5b** already points to a delocalization of the unpaired electron in *N*-pyrazolyl radicals; of course, generation of the radical from a 5-methylpyrazole derivative would be of interest. As the synthesis of reasonably pure **8** seemed to be very cumbersome (e.g., synthesis via **7b** and phosgene only gave ≤5% of **8;** vide supra), we considered the alternative pathway of photolyzing the isomeric 3- and 5-methyl-1-nitropyrazoles **14** and **15** (Scheme III), which can easily be obtained pure.[4] Indeed, preliminary experiments involving photolysis of 1-nitropyrazole in benzene showed the formation of both 1-phenylpyrazole (**9**) and biphenyl.[21] Hence, 5% solutions of **14** and **15** in benzene were irradiated with a Philips HP 125 lamp through a copper sulfate filter. The reactions were followed by GLPC. After 4 days, and a conversion of the *N*-nitropyrazoles of ~35%, in both solutions ~0.3 mol % of *N*-phenylpyrazoles was found. Though the yields were fairly low—thwarting accurate analysis—it can be stated that the ratio of isomeric *N*-phenylpyrazoles (**12:13**) was essentially the same in all samples, namely 4 ± 1.

Scheme III



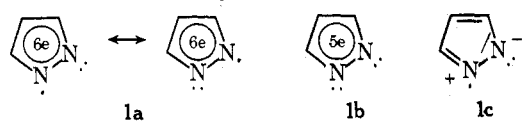
Other observations follow: the formation of **7b** as main reaction product; formation of nitrobenzene and of biphenyl; isomerization of the *N*-nitropyrazoles to *C*-nitropyrazoles (for both *N*-nitropyrazoles in a comparable isomer ratio); some isomerization **14** → **15** and **15** → **14,** respectively, much too slow, however, to account for the production of the two isomeric *N*-phenylpyrazoles **12** and **13** with the same ratio in both experiments.

As mutual isomerization of the *N-phenylpyrazoles* **12** and **13** is also very slow compared with their rates of formation (see Experimental Section), it appears that *N*-phenylpyrazoles are formed via the same intermediate. Considering the isomer ratio of 4:1, *which is equal to that obtained via perester decomposition,* this intermediate is most probably (again) the *N*-pyrazolyl radical.

Photolysis of *tert*-butyl 1-pyrazolepercarboxylates in benzene solution appeared to be very inefficient for the formation of *N*-phenylpyrazoles; e.g., irradiation of **5b** for 4 days only yielded ~0.1% of *N*-phenylpyrazoles. The use of a copper sulfate filter increased the yields somewhat, but the concentrations were still too low to permit an accurate analysis of the ratio of **12** and **13** formed.

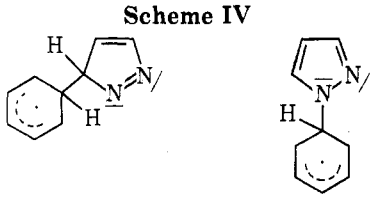
On the basis of the interpretation given above we may conclude that the unpaired electron in an *N*-pyrazolyl radical is delocalized over at least the two nitrogen atoms. It is not yet possible, however, to say anything definitive about the electronic structure in more detail. The exclusive formation of N-arylated pyrazoles, of course, tallies well with a σ-type structure **1a** (Chart IV). However, it cannot be excluded that a π-type structure **1b** obtains. A possible selective substitution reaction involving N only might be rationalized on thermodynamic grounds: attack by 1 on benzene via a C atom (exemplified in Scheme IV) must be followed by migration of an H atom, while attack with N directly gives the aromatic pyrazole ring, probably making the latter reaction more favorable. On the other hand, it is known that dialkylamino radicals do not react with benzene,[22] and give addition reactions with a relatively high activation energy;[23] hence we believe that *N*-pyrazolyl radicals are more aryl- (σ)- like.[24,25]

Chart IV



1a **1b** **1c**

Scheme IV



C-attack N-attack

From its competitive reaction with benzene and *p*-dichlorobenzene, it is seen that 1 has a pronounced electrophilic character. This is as might be expected, the reactive center being an electronegative atom. Moreover, resonance structure **1c** may contribute significantly to the polar properties of **1**, at least when it approaches the transition state involving a localized unpaired electron.

An ESR spectrum of 1 could be conclusive about its electronic structure, but as yet we were unsuccessful in obtaining a signal that can be ascribed to a pyrazolyl radical.[26]

It is clear that more work has to be done on the chemistry of *N*-pyrazolyl and related species like *N*-imidazolyl radicals, in order to elucidate their possible role as reacting intermediates, the possible occurrence of one-electron transfer processes, and their synthetic capabilities.

Experimental Section

General. NMR spectra were recorded on a JEOL-PS 100 or on a JEOL-Minimar 60-MHz instrument; unless otherwise stated, chemical shifts (δ) are expressed in parts per million relative to tetramethylsilane. Ir spectra were recorded on a Unicam SP 1200 or on a Beckman IR-10 spectrophotometer; mass spectra on an AEI-MS 902 apparatus. GLPC analyses were performed on Hewlett-Packard HP 5700 and on Varian Aerograph 1400 instruments, using a 44-m capillary OV-17 and a 2-m 4% OV-17 column, respectively. Elemental analyses were performed by Mr. W. J. Buys, TNO Laboratories of Organic Chemistry, Utrecht, The Netherlands. All melting points were uncorrected. For column chromatographic separations, the short-column technique of Hunt and Rigby[27] was used. Orienting thermolyses were carried out in sealed melting point tubes, inserted in the oil bath of a Büchi melting point apparatus; reaction products were analyzed by TLC and/or GLPC. Irradiations were performed on a cuvette scale; where indicated, a 1-cm copper sulfate (30% $CuSO_4 \cdot 5H_2O$) filter, which transmitted light with $\lambda > 320$ nm, was used.

Materials. Pyrazole (**7a**) and 3(5)-methylpyrazole (**7b**) were prepared by standard procedures; the synthesis of the *N*-nitropyrazoles **14** and **15** has been described in ref 15. The reference pyrazoles were either from the collection of Dr. Habraken, or prepared by standard procedures [e.g., 1-(2,5-dichlorophenyl)pyrazole from 2,5-dichlorophenylhydrazine and 1,1,2-trimethoxy-2-ethoxypropane[28]]. Other reference substances (e.g., isopropenyl methyl ether) were commercial products. *tert*-Butyl hydroperoxide was distilled under reduced pressure before use; dibenzoyl peroxide was recrystallized from chloroform. All other chemicals, being high-grade commercial products, were used as such.

1-Pyrazolecarbonyl Chloride (6a),[29,30] Phosgene was passed through a solution of pyrazole (**7a**, 10 g) in sodium-dried diethyl ether (150 ml) at 0°, until the initially formed white precipitate had disappeared (~2 hr). Dry nitrogen was passed through to remove the excess of phosgene; the solution was filtered and the major part of the solvent evaporated. The acid chloride, a white, crystalline solid, was isolated by filtration (14–18 g). Recrystallization from ether gave mp 53–54.5° (sealed melting point capillary); ir (Nujol) 1775 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.2 (d, 1, J = 3.0 Hz, 5-H), 7.85 (d, 1, J = 1.5 Hz, 3-H) and 6.55 (m, 1, 4-H).

The presence of an active Cl atom was substantiated by its immediate reaction with silver nitrate solution. The acid chloride appeared to be very reactive toward water and alcohols.

***tert*-Butyl 1-Pyrazolepercarboxylate (5a).** While stirring, solutions of **6a** (14.4 g) and of *tert*-butyl hydroperoxide (9.2 g), each in ~80 ml of sodium-dried ether, were added, slowly and simultaneously, to a cooled solution of pyridine (8.3 g) in ether (~50 ml); the temperature was kept at *ca.* −5°. The reaction mixture was stirred for 4 hr at room temperature and then filtered. The filtrate was washed successively with dilute hydrochloric acid and sodium carbonate solutions, dried over magnesium sulfate, and concentrated in vacuo, giving ~18 g of a colorless oil. The perester was purified by distillation under reduced pressure: bp 50° (0.10 mm); ir (liquid film) 1790 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.22 (d, 1, J = 3.0 Hz, 5-H), 7.83 (d, 1, J = 1.5 Hz, 3-H), 6.46 (m, 1, 4-H), and 1.42 [s, 9, $C(CH_3)_3$].

Anal. Calcd for $C_8H_{12}N_2O_3$: C, 52.16; H, 6.57; N, 15.21. Found: C, 51.88; H, 6.58; N, 15.37.

***tert*-Butyl 3-Methyl-1-pyrazolepercarboxylate (5b).** 3-Methyl-1-pyrazolecarbonyl chloride (**6b**) was prepared from 3(5)-methylpyrazole (**7b**) and phosgene according to von Auwers,[15] and was recrystallized from benzene: NMR ($CDCl_3$) δ 8.05 (d, 1, J = 3.0 Hz, 5-H), 6.38 (d, 1, J = 3.0 Hz, 4-H), and 2.39 (s, 3, CH_3).

From this acid chloride and *tert*-butyl hydroperoxide, perester **5b** was prepared as described above for **5a**. The residual colorless oil was distilled under reduced pressure: bp 60° (0.05 mm); ir (liquid film) 1785 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.99 (d, 1, J = 3.0 Hz, 5-H), 6.23 (d, 1, J = 3.0 Hz, 4-H), 2.26 (s, 3, CH_3), and 1.41 [s, 9, $C(CH_3)_3$]; signals at 7.59 and 2.59 ppm pointed to the presence of ~4% of the 5-methyl isomer **8**.

Anal. Calcd for $C_9H_{14}N_2O_3$: C, 54.53; H, 7.12; N, 14.13. Found: C, 54.58; H, 7.11; N, 14.25.

Thermal Decomposition of 5a in Benzene. A. An ampoule containing a weighed amount (~0.2 g) of **5a** dissolved in a tenfold quantity of benzene was degassed and sealed. The tube was placed in an oven at 135° for 1 hr; a known amount of hexamethyldisiloxane (HMDS) was added to the cooled contents and a quantitative NMR analysis was then made for *tert*-butyl alcohol (1.07 ppm relative to HMDS), acetone (1.47 ppm), toluene (2.00 ppm) and isopropenyl methyl ether (1.65 and 3.10 ppm). The identity of the compounds mentioned was ascertained by adding small amounts of the authentic materials, and by GLPC.

B. Solutions of **5a** in benzene (1 and 10%, respectively) were

thermolyzed in an autoclave under a nitrogen atmosphere. After heating at 135° for at least 1 hr, benzene was carefully removed by distillation; the products were then separated by column chromatography on silica gel (H, according to Stahl), eluting with benzene–ethyl acetate–methanol mixtures of increasing polarity. Collected fractions were compared with reference materials on TLC, concentrated, and investigated further with the aid of NMR and mass spectrometry; in addition, GLPC on a packed OV-17 column was used to test the possible presence of C-phenylated pyrazoles.

Thermal Decomposition of 5a in a Benzene–*p*-Dichlorobenzene Mixture. A solution of 52 mg of perester **5a** in 0.90 g of a 1:10 molar mixture of *p*-dichlorobenzene and benzene was heated in a sealed tube for 1.5 hr at 135°. The formation of 1-(2,5-dichlorophenyl)pyrazole and of 1-phenylpyrazole (**9**) was demonstrated, and their ratio was determined by GLPC analysis on a packed OV-17 column.

Phenylation of Pyrazole (7a) with the Aid of Dibenzoyl Peroxide. An ampoule containing a mixture of dibenzoyl peroxide (0.25 mmol), **7a** (1.13 mmol), and benzene (11.3 mmol) was degassed, sealed, and heated (0.3 hr at 135°). GLPC analysis on a packed OV-17 column revealed the presence of biphenyl (~0.4 mol/mol dibenzoyl peroxide), 3(5)-phenylpyrazole (0.025 mol/mol biphenyl), and 1-phenylpyrazole (**9**, 0.010 mol/mol biphenyl), in addition to several other products. As the presence of 4-phenylpyrazole could not be detected, the partial rate factor given for the 4 position must be considered as an upper limit.

Phenyl 1-Pyrazolecarboxylate (11). Preparation and Thermal Stability. Pyrazole (**7a**, 2.3 g) was slowly added to 5.3 g of phenyl chloroformate; the mixture was then heated at 110° for 1.5 hr, diluted with water, and neutralized with sodium carbonate, and the phenyl ester was isolated via extraction with ether, crude yield 5.3 g (83%). Crystallization from hexane gave pure **11**: white crystals; mp 47–48.5°; ir (KBr) 1780 cm^{-1} (C=O); NMR ($CDCl_3$) δ 8.5 (d, 1, J = 3 Hz, 5-H), 8.0 (d, 1, J = 1.5 Hz, 3-H), 7.5 (m, 5, C_6H_5), and 6.6 (m, 1, 4-H).

Anal. Calcd for $C_{10}H_8N_2O_2$: C, 63.82; H, 4.29; N, 14.89. Found: C, 63.89; H, 4.37; N, 14.91.

This phenyl ester appeared to be stable upon heating at 200° for 5 min (TLC analysis).

Thermal Decomposition of *tert*-Butyl 3-Methyl-1-pyrazolepercarboxylate (5b) in Benzene. A. A solution of 3.0 g of **5b** in 150 ml of benzene was heated in an autoclave at 150° for 1 hr. The resulting solution was carefully concentrated and the reaction products were separated by column chromatography as described for the thermolysis of **5a**. The fractions were analyzed with the aid of TLC and NMR spectroscopy. In this way, the *N*-phenylpyrazoles **12** and **13** (eluted in that order) were obtained in a reasonably pure form.

B. In a sealed tube, a 2.4% solution of **5b** in benzene (containing 0.01% of *p*-di-*tert*-butylbenzene as internal standard) was heated at 150° for 1 hr; the reaction products were analyzed by GLPC. A capillary OV-17 column was used for the separation of the two *N*-phenylpyrazoles **12** and **13**; their ratio was calculated to be 5:1. In addition, a packed OV-17 column was used in searching for C-phenylated pyrazoles: no detectable amounts of 3(5)-methyl-4-phenyl- or of 3(5)-methyl-5(3)-phenylpyrazole were present.

C. Control Experiment. A benzene solution of a mixture of **12** and **13** was heated in a sealed tube at 150° for 1 hr; NMR analysis showed that the composition of the mixture remained unchanged.

Photolysis of the *N*-Nitropyrazoles 14 and 15 in Benzene Solution. A. In 1.0-cm quartz cuvettes, solutions of 3-methyl-1-nitropyrazole (**14**) and of 5-methyl-1-nitropyrazole (**15**), respectively (both 5% in benzene, and containing 0.01% of *p*-di-*tert*-butylbenzene as internal standard), were irradiated through a copper sulfate filter employing a 175-W Philips HP lamp. Samples were taken at 6, 24, and 96 hr, and analyzed by GLPC using a capillary OV-17 column. In addition, a packed OV-17 column was used for the analysis of C-nitropyrazoles; in order to prevent thermal isomerization of the residual *N*-nitropyrazoles, the injection port had to be kept at ≤130°.

B. Control Experiment. A benzene solution of a mixture of the *N*-phenylpyrazoles **12** and **13** was irradiated (copper sulfate filter) for 96 hr; NMR analysis showed that their molar ratio had changed from 0.44 to 0.74.

Photolysis of the *tert*-Butyl Peresters 5a and 5b in Benzene Solution. A. Photolysis of the unsubstituted perester **5a** was studied qualitatively by following the reaction by TLC: when a 2.5% solution of **5a** in benzene was irradiated, small amounts of 1-phenylpyrazole (**9**) and of biphenyl could be detected. After 3 days a considerable amount of starting material **5a** was still present.

B. Photolysis of a 2.4% solution of the 3-methyl substituted perester **5b** in benzene (containing 0.01% of *p*-di-*tert*-butylbenzene as internal standard) was performed both with and without a copper sulfate filter. After 96 hr, the resulting solutions were analyzed by GLPC on a capillary OV-17 column. In either case biphenyl was found and, in only small quantities, the isomeric *N*-phenylpyrazoles **12** and **13** (molar ratios ca. 9:1).

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Registry No.—**5a**, 53881-36-0; **5b**, 53881-37-1; **6a**, 53355-55-8; **6b**, 53881-38-2; **7a**, 288-13-1; **7b**, 1453-58-3; **9**, 1126-00-7; **11**, 53881-39-3; **12**, 1128-54-7; **13**, 6831-91-0; **14**, 31163-84-5; **15**, 31163-85-6; phosgene, 75-44-5; *tert*-butyl hydroperoxide, 75-91-2; phenyl chloroformate, 1885-14-9; 1-(2,5-dichlorophenyl)pyrazole, 53881-40-6.

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Ion-Pair Return Associated with Solvolysis of 1,2-Dimethyl-*exo*-2-norbornyl *p*-Nitrobenzoate-^{18}O[1]

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Solvolysis of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (I-OPNB) in 90% aqueous acetone involves exclusive alkyl–oxygen cleavage and is accompanied by ion-pair return which results in racemization of optically active I-OPNB and randomization of the carboxyl oxygen atoms of ^{18}O-labeled I-OPNB. In this system the carbonium ion is not symmetrical and k_{rac} corresponds to an upper limit of 37% of the total return from product-forming intermediates. The relative rates of racemization and carboxyl oxygen equilibration indicate that k_{eq} corresponds to ~20% of the total return.

Several methods for detecting ion-pair return associated with SN1 solvolytic reactions have been reported. These include salt effects,[2,3] isomerization of the cation[2b,4,5] or anion,[6] racemization of the unsolvolyzed substrate,[2b,5,7] randomization of carboxyl or sulfoxyl oxygen atoms,[5,8] and secondary deuterium isotope effects.[9] To determine the amount of return requires an independent measure of (a) the total rate of ionization or (b) the rate of re-formation of substrate by ion-pair return.

With optically active substrates that give symmetrical (bridged[2b,8b] or allylic[7,10]) carbonium ions, the rate of loss of optical activity (eq 1) corresponds to the total rate of ionization providing that the ion pair, as well as the unperturbed cation, is symmetrical. With systems that do not isomerize, ion-pair return does not disturb the rate of solvolysis (eq 2) and the rate of return, which corresponds to rate of racemization (eq 3), is obtained indirectly as the difference between rates of ionization (k_α) and solvolysis (k_t), i.e., $k_{rac} = k_\alpha - k_t$.[10] Alternatively, the rate of racemization can be obtained directly by isolating samples of unsolvolyzed substrate throughout the reaction and determining k_{rac} from the rotations.[8a]

Another direct method for measuring return is determining the rate of randomization of carboxyl or sulfonate oxygen atoms (k_{eq}) starting with discretely ^{18}O-labeled *p*-nitrobenzoate[8a,10] (eq 4) or arylsulfonate.[8b] Providing the oxygen atoms in the anion are equivalent in the ion-pair intermediate, k_{eq} corresponds to total return. The distinguishing feature of this method is that it is applicable to achiral as well as chiral nonrearranging systems.

$$(+)\text{-RX} \xrightarrow{k_\alpha} \text{inactive products} \quad (1)$$

$$\text{R–X} \xrightarrow{k_t} \text{solvolysis products} \quad (2)$$

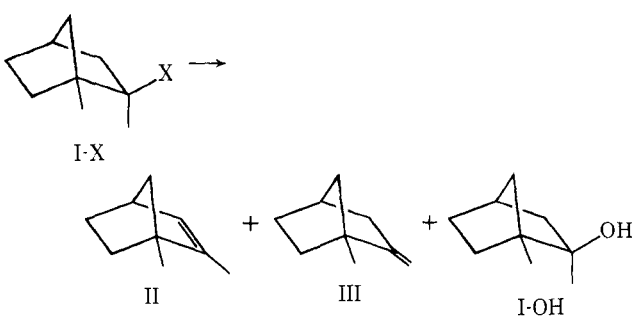
$$(+)\text{-RX} \xrightarrow{k_{rac}} (\pm)\text{-RX} \quad (3)$$

$$\text{R—}^{18}\text{OCOAr} \xrightarrow{k_{eq}} \text{R—}^{18}\text{OC}^{18}\text{OAr} \quad (4)$$

Since the oxygen atoms in the intermediate are not always equivalent,[12] k_{eq} is a lower limit for return—excess rebonding of the original oxygen and carbon atoms is undetected. Similarly, k_α is a lower limit for ionization (or k_{rac} for return) because even though the unperturbed bridged or allylic cation is symmetrical the ion pair may not be. Indeed, there is evidence that this is the case in some allylic systems.[13]

To obtain information regarding the fraction of return detected by oxygen equilibration we have compared k_{eq} with return measured by independent methods in allylic systems and systems involving symmetrical bridged cations.[8b] For *p*-nitrobenzoates the amount of equilibration associated with return ranges from nil for a case involving rearrangement to a strained carbonium ion[14] to partial for several allylic systems[10] and one rearranging system in which the anion migrates a considerable distance,[15] and evidently to complete in systems that give relatively stable (delocalized) carbonium ions.[5,10b,12]

We now report a comparison of k_{eq} with an independent measure of a lower limit of return for solvolysis of 1,2-dimethyl-*exo*-2-norbornyl *p*-nitrobenzoate (I-OPNB), a system which does not involve a symmetrical bridged ion but one in which ion-pair return results in racemization of the unsolvolyzed ester.[11]



I-X II III I-OH

The pertinent rate constants for solvolysis of I-OPNB in 90% aqueous acetone at 78° are shown in Table I. The titrimetric rate constants (k_t) were steady up to 80% solvolysis, which shows that the structure of the substrate is preserved throughout the reaction. A control experiment with ether-^{18}O labeled I-OPNB showed that solvolysis involves exclusive alkyl–oxygen cleavage.

For the polarimetric experiments the solvent contained a 50% excess of 2,6-lutidine to neutralize the acid produced