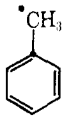
drogen atoms attain almost complete equivalence in the molecular ion of toluene, and that a single ^{13}C atom in position α[2] or 1[3,4]—or 2, as shown in the present work—is lost statistically in the path leading to $C_5H_5^+$ ions. Carbon-13 label retentions in the $C_5H_5^+$ ion (eq 1) derived from toluene-α,1-$^{13}C_2$ (I)[3,4] further indicated that

$$C_7H_8\cdot^+ \xrightarrow{-H\cdot} C_7H_7^+ \xrightarrow[m^* = 46.4]{-C_2H_2} C_5H_5^+ \qquad (1)$$

the tropylium ion formed is best represented as one in which the carbon atoms have all lost positional identity related to their toluene origin, *i.e.*, a randomized tropylium ion (II). The latter may arise (a) by a series of



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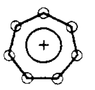

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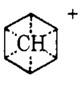

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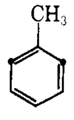
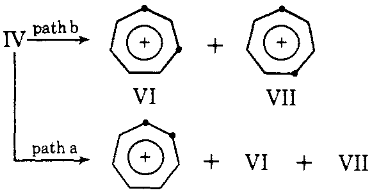


IV

rapid benzyl ion–tropylium ion isomerizations, (b) by insertion of the methyl carbon atom randomly between adjacent carbon atoms of the ring (III), or (c) by an even more complex mechanism. Toluene-α,1-$^{13}C_2$, while able to distinguish between a randomized tropylium ion and one formed by insertion of the methyl carbon atom between C_1 and C_2, does not differentiate between processes a and b. It was hoped that the data obtained from a dilabeled toluene, such as IV, in which the labeled carbon atoms were not adjacent, would enhance an understanding of the processes involved.

Synthesis of IV proceeded from 1,3-dibromopropane and sodium cyanide-^{13}C followed by hydrolysis of the resulting dinitrile[5] to glutaric acid-1, 5-$^{13}C_2$, which was converted successively to the diol with lithium aluminum hydride, and to the dibromide by the action of phosphorus tribromide. The dibromide was converted to toluene by a modification[4] of the procedure of Rieker.[6] Owing to the isotopic impurity in IV, it was necessary to synthesize toluene-2-^{13}C. This was accomplished by treatment of γ-butyrolactone with sodium cyanide-^{13}C followed by hydrolysis to glutaric acid-1-^{13}C.[7] Conversion of the latter to toluene was achieved by the procedure cited above. High-resolution spectra were recorded on an AEIMS-9 mass spectrometer at a resolution of 18,000 (10% valley definition); the data represent averages of 20 readings.

The tropylium ions expected from IV *via* paths a and b are shown in eq 2. Loss of C_2H_2 from path a tropylium ions (V–VII) would give (0.048) $C_5H_5^+$, (0.476) $^{13}CC_4H_5^+$, and (0.476) $^{13}C_2C_3H_5^+$. Loss of C_2H_2 from path b tropylium ions (VI and VII) would give (0.000) $C_5H_5^+$, (0.571) $^{13}CC_4H_5^+$, and (0.429) $^{13}C_2C_3H_5$. No $^{13}C_2H_2$ can be expelled in the latter case since the labeled carbon atoms are always one or two carbon atoms removed from each other. Therefore, no unlabeled



(2)

$C_5H_5^+$ ions should be formed if path b alone is operative. However, label retentions shown in Table I reveal the presence of unlabeled $C_5H_5^+$ ions, *i.e.*, the data do not agree with the distribution expected for a tropylium ion formed by path b. In fact, the observed retentions compare favorably with those for I,[3] which are close to the values expected for the completely randomized tropylium ion (II).

Table I. High-Resolution Mass Spectral Peaks

		Rel abundance[b–d]	
m/*e*	Composition[a]	Toluene-2-^{13}C[e]	Toluene-2,6-$^{13}C_2$[f]
65	C_5H_5	0.302	0.057
66	$^{13}CC_4H_5$	0.698	0.467
67	$^{13}C_2C_3H_5$		0.476

[a] Other isobaric hydrocarbon ions omitted. [b] $\Sigma = 1.000$. [c] Corrected for naturally abundant ^{13}C. [d] Calculated for 100% isotopic enrichment. [e] Sample contained 51.9% labeled toluene. [f] Sample contained 49.9% singly labeled, 23.1% unlabeled, and 27% doubly labeled toluene.

Hence, it may be concluded that the $C_7H_7^+$ ion derived from toluene is not formed by path b, but rather by a mechanism in which all the carbon atoms have lost positional identity with respect to each other. The data do not rule out the occurrence of path b; they simply show that if path b does occur, it must be accompanied by another path, say a, which would result in total scrambling of all the carbon atoms. Further study of these and other ions in the spectrum of IV is under investigation.

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Received April 10, 1970

Intramolecular Nitrone–Allene Cycloadditions[1]

Sir:

The utility of 1,3-dipolar cycloaddition reactions for the synthesis of five-membered ring heterocycles is well documented.[2] Studies reported from this laboratory have revealed examples of the intramolecular cycloaddition of nitrones to olefins.[3] However, few data relate the use of allenes as dipolarophiles in such reactions. We wish to disclose that the intramolecular cyclization of a series of allenic nitrones has been accomplished which results in the formation of several novel bicyclic products.

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(3) K. L. Rinehart, Jr., A. C. Buchholz, G. E. Van Lear, and H. L. Cantrill, *J. Amer. Chem. Soc.*, 90, 2983 (1968).

(4) For a comprehensive study on the tropylium ion derived from ^{13}C labeled benzyl-type compounds, see A. S. Siegel and K. L. Rinehart, Jr., 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 7-12, 1969, Abstract ORGN 66.

(5) M. Kushner and S. Weinhouse, *J. Amer. Chem. Soc.*, **71**, 3558 (1949).

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(8) Research Associate and Fellow of Mellon Institute.

(1) Acknowledgment is made to the National Science Foundation for support of this work, under Grant No. GP 14114.

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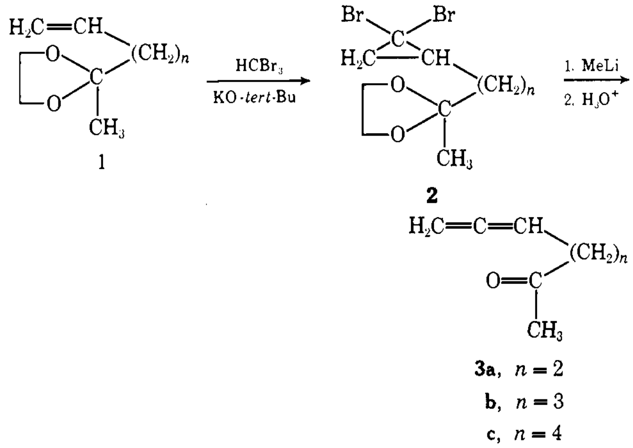
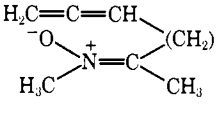
(3) N. A. LeBel, M. E. Post, and J. J. Whang, *J. Amer. Chem. Soc.*, **86**, 3759 (1964), and earlier references.

The allenic methyl ketones **3** (n = 2–4) were synthesized by application of the method of Crandall and Mayer[4] to the appropriate olefinic ketals **1**. Condensation with dibromocarbene gave the 1,1-dibromocyclopropane adducts **2**, which when treated with methyllithium followed by mild acid hydrolysis gave the desired products **3**.[5,6]



When a solution of *N*-methylhyroxylamine hydrochloride in ethanol containing 1 equiv of sodium acetate was treated with 5,6-heptadien-2-one (**3a**) in refluxing ethanol for 12 hr a basic product (98% pure by vpc), **5**, was isolated in 45% yield. Assignment of this product as the unsaturated bicyclic isoxazolidine **5** was suggested by its nmr and ir spectra, and catalytic hydrogenation (10% Pd–C in ethanol) gave the known saturated isoxazolidine **6**.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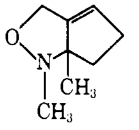
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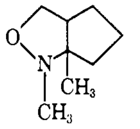
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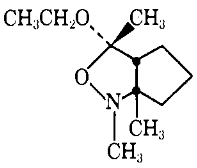
Clearly, the nitrone **4a** was the intermediate, and **5** arose by intramolecular cycloaddition at the *terminal* double bond of the allenic function. The exclusive orientation observed in this reaction is not surprising, since the alternative mode of closure would have produced a more strained 4-methylene-3-oxa-2-azabicyclo[3.2.0]heptane system. That this latter system was not formed reversibly under the reaction conditions is suggested by our failure to detect products from the addition of ethanol to the *exo*-methylene double bond (*vide infra*).

Similarly, 6,7-octadien-2-one (**3b**) was converted to the *N*-methylnitrone **4b** in ethanol, and cyclization occurred *in situ*. The volatile basic products (65%) showed three components by vpc[6] in the ratio 44:16:40. These were separated by column chromatography and identified as **7**, **8**, and **9**, respectively. The similar spectral characteristics to those of **5** and hydrogenation to the known dihydro compound[3] served to characterize the component **9**. Mass spectra and nmr analysis showed that **7** and **8** were epimers and that their compositions were those of a bicyclic adduct *plus* ethanol.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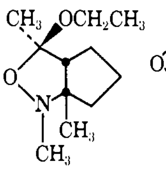
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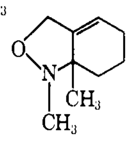
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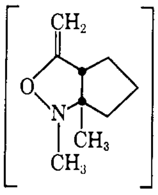
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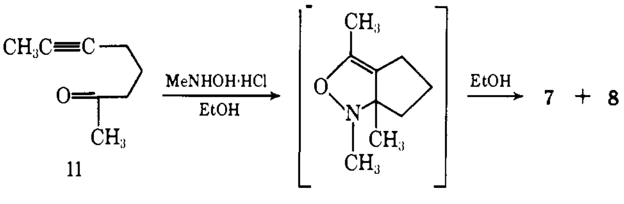

No structures other than **7** and **8** are in accord with the observed properties. In both compounds the methylene hydrogens of the ethoxy group exhibit a complex multiplet at δ 3.3 typical of a pair of diastereotopic protons. The stereochemical assignments to **7** and **8** were made on the basis of the relative chemical shifts of the C_1 and C_4 methyl groups in the nmr spectra (for **7**, C_4–Me, 66 Hz; C_1–Me, 60 Hz; C_5–H and C_6–H, 100–130 Hz; for **8**, C_1–Me and C_4–Me, 70 and 68 Hz). Additionally, when the acetylenic ketone **11** (semicarbazone mp 118–119°) was allowed to react with *N*-methylhydroxylamine hydrochloride under identical conditions, compounds **7** and **8** were detected in the ratio 92:8, respectively. These were the major isolated products under these reaction conditions.[7,8]

These data suggest that the 4-*exo*-methylene isoxazolidine **10** was the major, primary cyclization product of **4b**, resulting from addition to the *internal* double bond of the allenic group. Subsequent acid-catalyzed addition of ethanol led to the isolated ketals **7** and **8** (a similar reaction must also occur with **12**). Compound **10** has not been isolated as yet. Further demonstration of its relative instability was indicated by the reaction between **3b** and purified *N*-methylhydroxylamine in refluxing benzene or toluene. Only compound **9** was detected (25%), and much polymer formation was noted.

Treatment of 7,8-nonadien-2-one (**3c**) with *N*-methylhydroxylamine hydrochloride in ethanol did not lead to characterizable products. However, when the reaction of **3c** was run in benzene or toluene with *N*-methylhydroxylamine, one major cycloadduct was isolated in 15% yield. This compound was readily identifiable as **13** by its nmr (doublet of doublets at 300 Hz, *exo*-methylene), ir, and mass spectra. Two other basic materials were formed, but these apparently are not the result of normal cycloaddition and they remain unidentified.

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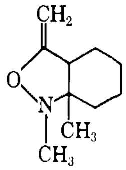
(5) New compounds were identified by their nmr, ir, and mass spectra. Nmr spectra were obtained with a Varian T-60 spectrometer as solutions in carbon tetrachloride (or neat) with TMS as the internal standard. Mass spectra were determined with a AEI MS-902 double focusing spectrometer at 70-eV ionization potential and 100-μA emission.

(6) Vpc analyses were performed on an HP 5750 dual flame ionization unit, with a 6 ft × $^1/_8$ in. aluminum column containing 8% (w/w) Dow Polyglycol E-20M on Chromosorb W.

(7) The results of the intramolecular cycloaddition of acetylenic nitrones will be reported later.

(8) A 4-isoxazoline such as **12** could be expected to undergo valence rearrangement according to the first step in the scheme put forth by J. E. Baldwin, R. G. Pudussery, A. K. Qureshi, and B. Sklarz, *J. Amer. Chem. Soc.*, **90**, 5325 (1968). The other (minor) components in the reaction mixture here described have not been characterized.



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In summary, our findings demonstrate an important extension to 1,3-dipolar additions of nitrones which impart added and predictable functionality through the use of cumulated double bonds. The special reactivity displayed by the products generated in this study are being further explored.

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Received May 19, 1970

Photoreactivity of p-Methoxyphenyl Ketones. Evidence for Hydrogen Abstraction from Equilibrium Concentrations of Upper n,π^* Triplets

Sir:

The difference in photoreactivity between aryl ketones with n,π^* lowest triplets and those with π,π^* lowest triplets has posed one of the oldest continuing problems in modern photochemistry.[1] Three years ago, Yang, McClure, and coworkers reported that several ring-substituted acetophenones undergo photoreduction with reasonable quantum efficiencies even though all spectroscopic evidence indicates that their lowest triplets are mostly π,π^* in nature.[2] Later, Yang[3] and we[4] both showed that methyl and methoxy substituents decrease the apparent reactivity of ketone triplet states in hydrogen abstraction reactions. Elegant spectroscopic investigations in several laboratories have established (1) that the "n,π^*" and "π,π^*" triplets of such phenyl alkyl ketones lie within a few kilocalories of each other, and (2) that the two states mix vibronically.[5] Consequently, Yang suggested[3] that the hydrogen abstraction reactions of the substituted phenyl ketones occur from the lowest triplet, which is mostly π,π^* in character but has enough n,π^* character to be *slightly* reactive. We originally felt[6] that mixing of states might be a chief determinant of triplet state reactivity and agreed that Yang's appealing suggestion was possible. However, there has been no evidence presented which eliminates the possible involvement of the upper n,π^* triplets. Since these are known to be reactive in hydrogen abstraction, and since the two states are so close together that they may well equilibrate thermally before decaying, this alternate possibility could not be dismissed.[4] We now present evidence that strongly suggests that the majority of hydrogen abstraction by p-methoxyphenyl alkyl ketones occurs from the upper ^{3}n,π^* state.

Equations 1–3 describe the quantum yield for type II photoelimination when only the lower triplet reacts, only the upper triplet reacts, or both react, respectively. In all cases, P_p represents the probability that the

$$\Phi = k_r^{\pi}\tau^{\pi}P_p = P_pk_r^{\pi}/(k_r^{\pi} + k_d^{\pi}) \tag{1}$$

$$\Phi = X_nk_r^{n}\tau_{eq}P_p = P_pX_nk_r^{n}/(X_nk_r^{n} + X_{\pi}k_d^{\pi}) \tag{2}$$

$$\Phi = (X_nk_r^{n} + X_{\pi}k_r^{\pi})\tau_{eq}'P_p = P_p(X_nk_r^{n} + X_{\pi}k_r^{\pi})/[X_nk_r^{n} + X_{\pi}(k_r^{\pi} + k_d^{\pi})] \tag{3}$$

1,4-biradical intermediate goes on to products;[7] the k_r's represent rate constants for hydrogen abstraction by the two states; k_d^{π} represents the rate of radiationless decay of the π,π^* triplet (k_d^{n} is thought to be negligibly small compared to k_r^{n});[7] X_n and X_{π} represent the fractions of n,π^* and π,π^* states populated at thermal equilibrium; and the excited state lifetimes are defined by the denominators of the right-hand equations. A Stern–Volmer quenching plot is linear in every case, *as long as there is not so much quencher present as to upset the equilibration of states.*

Determination of Φ and τ values allows one to estimate *apparent* k_r values but does not allow one to distinguish among the three kinetic possibilities. Variations in apparent k_r values as a function of the energy gap between the two triplets would be too subtle to interpret at present, because both X_n and k_r^{π} (proportional to the amount of state mixing) would decrease as ΔE increases. Moreover, accurate spectroscopic determination of ΔE values is by no means straightforward. Consequently, we have applied a more classic test and determined how the selectivity of the excited ketone depends on its reactivity.

Table I contains photokinetic data for five phenyl alkyl ketones containing different kinds of γ C–H bonds; Table II presents data for the analogous p-anisyl ketones. These data were all acquired by our usual method[7] of Stern–Volmer quenching with 2,5-dimethyl-2,4-hexadiene in degassed benzene solutions at 25°.

Table I. Photoelimination of Select Phenyl Ketones $PhCOCH_2CH_2R$[a]

	R	Φ_{II}[b]	$k_q\tau$, M^{-1} [c]	k_r^{n}, 10^7 sec^{-1} [d]	Rel k_r
P1	CH_3	0.36	660	0.8	(1)
P2	CH_2CH_3	0.33	40	12.5	16 (1)
P3	$CH(CH_3)_2$	0.25	11	45.0	60
P4	$CH_2CH_2CO_2CH_3$	0.64	125	4.0	0.32
P5	CH_2CH_2CN	0.46	500	1.0	0.08

[a] 0.10 *M* ketone solutions irradiated at 3130 Å to 5% conversion. [b] Quantum yield of acetophenone formation in benzene. [c] Slope of Stern–Volmer quenching plot; all averages of duplicate runs. [d] $k_r^{n} = 1/\tau$, k_q assumed to equal 5×10^9: W. D. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969); G. Porter and M. R. Topp, *Proc. Roy. Soc., Ser. A*, **315**, 163 (1970).

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(3) N. C. Yang and R. L. Dusenbery, *ibid.*, **90**, 5900 (1968).

(4) P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5898 (1968).

(5) (a) D. R. Kearns and W. A. Case, *ibid.*, **88**, 5087 (1966); (b) A. A. Lamola, *J. Chem. Phys.*, 47, 4810 (1967); (c) R. M. Hochstrasser and C. Marzzacco, *ibid.*, **49**, 971 (1968); (d) E. C. Lim, R. Li, and Y. H. Li, *ibid.*, **50**, 4925 (1969); (e) E. C. Lim, Y. Kanda, and J. Stanislaus in "Molecular Luminescence," E. C. Lim, Ed., W. A. Benjamin, New York, N. Y., 1968, p 111.

(6) P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

(7) P. J. Wagner and A. E. Kemppainen, *ibid.*, **90**, 5896 (1968).