stituted benzene ring, whereas those from nitrobenzene were evidently more energetic and showed no discrimination. Arylation of benzenes containing chlorine and other substituent groups is being studied and the isomer ratios are being determined for comparison with those formed at low temperatures in solution.[19]

[19] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y. 1957, p 484.

Registry No.—Nitrobenzene, 98-95-3; fluorobenzene, 462-06-6; *p*-difluorobenzene, 540-36-3; benzotrifluoride, 98-08-8; hexafluorobenzene, 392-56-3; benzene-d_6, 1076-43-3; benzoyl peroxide, 94-36-0.

Acknowledgment.—The authors are indebted to D. K. Albert of the American Oil Co. for his assistance in gas chromatographic analyses.

Photochemistry of Some Dicyclopentadiene Derivatives

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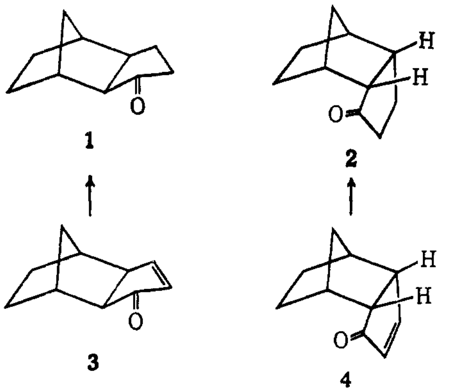
Received March 24, 1967

Photolysis of either *exo* or *endo* tricyclic ketones **1** or **2** led to β-(2-norbornenyl)propanal (**5**) as the major primary photoproduct. A secondary product was the *endo*-oxetane **6** formed *via* intramolecular photocycloaddition of **5**. Photorearrangement of epoxy ketone **11** yielded diketone **12** by hydrogen migration.

Photochemically induced reactions of ketones have been the subject of intensive investigations.[1] The unique synthetic possibilities in this area stimulated our interest in the examination of the behavior of some polycyclic ketones.[2] As a secondary consideration, it was anticipated that the rigid geometry inherent in these systems might provide information on the stereochemical requirements of some of the competing processes. This paper reports the results of studies with some derivatives of dicyclopentadiene. In particular, the *exo* and *endo* ketones **1** and **2** and the epoxy ketone **11** were investigated.[3]

Results

The required ketones **1** and **2** were prepared by catalytic reduction of the corresponding α,β-unsaturated systems **3** and **4**.[4]



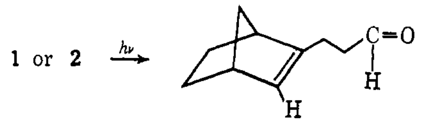
1 **2** **3** **4**

Solutions of **1** or **2** were irradiated (dioxane–water) through Pyrex filters with medium-pressure, mercury-vapor sources. Disappearance of starting ketones was accompanied by the formation of two new materials. As the reaction progressed, it was apparent that one of the photoproducts was formed from the other in a secondary reaction. Prolonged irradiation led to a single product at the expense of both the starting material and the primary photoproduct.

For isolation purposes, the reaction was discontinued when the ratio of the two new products was *ca.* 2:1. At this point most (>95%) of the starting material had been consumed.

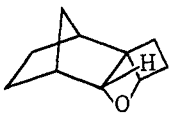
The two components were isolated by gas chromatography and characterized as described below. The primary product displayed a strong carbonyl absorption band at 5.77 μ, double-bond absorptions at 6.15 and 11.53 μ, and an aldehyde C–H stretching vibration at 3.68 μ. The integrated nmr spectrum revealed one olefinic proton at τ 4.48 and an aldehyde proton at 0.34.

These data, and the fact that both **1** and **2** led to the same product, leave little doubt that the primary product has structure **5**.



5

The nature of the secondary photoproduct was deduced from the absence of carbonyl absorption in the infrared spectrum and the presence of a strong absorption band at 10.06 μ.[5] These data and literature analogies[6] suggested an oxetane structure for this substance. The two most likely alternatives appeared to be **6** and **7**. A secondary carbinol was obtained on reduction of the oxetane with lithium aluminum hydride.[7] Of the four possible alcohols derivable from



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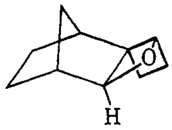

7

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[1] For a general survey, see J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, Chapter 5.

[2] An excellent bibliography may be found in R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., New York, N. Y., 1966, Chapter 3.

[3] Photolysis of the unsaturated ketone **4** in dilute solution led only to high-melting materials, presumably dimeric in nature. Unpublished observations of A. S.

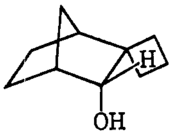
[4] K. Alder and G. Stein, *Ann.*, **504**, 205 (1936). P. D. Bartlett and A. Schneider, *J. Am. Chem. Soc.*, **68**, 6 (1946).

[5] G. M. Barrow and S. Searles, *ibid.*, **75**, 1175 (1953).

[6] W. L. Dilling, *Chem. Rev.*, **66**, 373 (1966).

[7] S. Searles, Jr., K. A. Pollart, and E. F. Lutz, *J. Am. Chem., Soc.* **79**, 948 (1957).

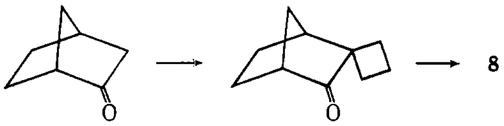
6 and 7, the nmr spectrum seemed most consistent with formula 8 in that the carbinol proton appeared



8

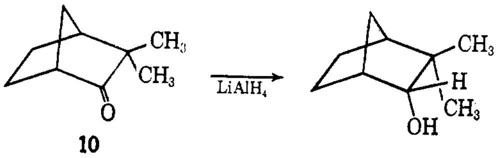
as a clean doublet (J = 4.5 cps).[8] This alcohol could only originate from the *endo*-oxetane 6, but it was desirable to provide a less ambiguous structure proof.

A synthetic scheme was devised for 8 which involved preparation and reduction of the spiro ketone 9 (eq 1).



9 (1)

Alkylation of norcamphor with trimethylene dibromide led to low yields of 9. Reduction of 9 with lithium aluminum hydride produced 8 and minor amounts ($<10\%$) of another material. Since camphenilone 10 is attacked by complex hydrides predominantly from the *exo* direction,[9] there is no reason to believe that 9 would not also suffer *exo* attack. Hence, the photoproduct has the *endo* structure 6.[10]



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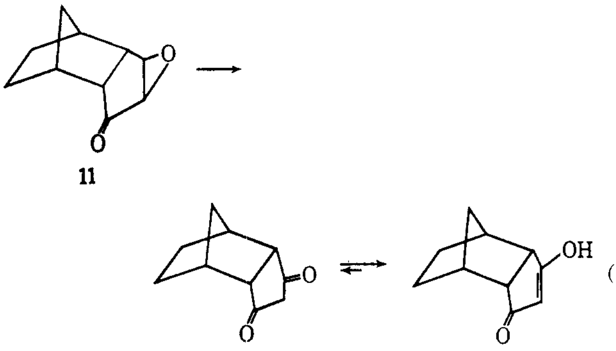
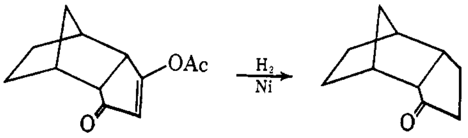
An investigation of the epoxy ketone 11 was also undertaken. The possibility of ring contraction of 11 to a tricyclo$[4.2.1.0^{2,5}]$nonane derivative was an attractive alternative in this system.[11] Unfortunately, the only product isolated from this reaction was 12,[12] which exists mainly in the enolic form 13 (eq 2).



11

12 **13** (2)

The physical properties of 13 agreed well with literature values and catalytic hydrogenation of the enol acetate 14 yielded ketone 2 as the major product. These data adequately define the structure of 13.



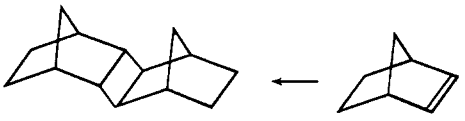
14 **2**

Discussion

Formation of aldehyde 5 from both the *exo* and *endo* ketones, while not wholly anticipated,[13] is unexceptional.

The observed *endo* attack of the carbonyl group in the formation of the oxetane is unprecedented. Intermolecular photoadditions of carbonyl compounds to norbornenes have invariably led to predominant, if not exclusive, *exo* attack.[14]

The *endo* selectivity observed is probably partly a result of the radical character of the excited carbonyl group,[15] but we can see no obvious reason why nonbonded, torsional, or bond-angle differences would favor *endo* over *exo* attack. It is interesting that sensitized[16] dimerization of norbornene leads to 88% of the *endo-trans-exo* system 15.



15

Presumably, this reaction involves addition of triplet norbornene to ground-state norbornene. Our stereochemical results would be consistent with norbornene dimerization if intramolecular energy transfer from the exited carbonyl group to the double bond occurred prior to addition.[17]

The important question of what factors determine the unique stereochemistry of these cycloaddition reactions, is yet to be answered.

Experimental Section

Analyses were by Micro-Tech Labs, Skokie, Ill. Infrared spectra were determined in carbon tetrachloride or as noted on a Beckman IR-5A spectrophotometer. Nuclear magnetic resonance spectra were obtained from a Varian Model A-60 spectrometer in carbon tetrachloride with internal tetramethylsilane. Gas chromatograms were obtained with an Aerograph Model A90P instrument. Columns were 0.25 in. (o.d.) packed with 10–15% liquid phase on Chromosorb G. Carbowax 20 M is abbreviated as Carbowax. Capillary gas chromatograms were determined on a Barber–Colman Model 5000 instrument with a flame ionization detector. Columns available were

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[8] P. von R. Schleyer, W. E. Watts, and C. Cupas, *ibid.*, **86**, 2722 (1964) report similar values ($J \sim 5$ cps) for *endo*-camphenilyl systems.

[9] S. Beckmann and R. Mezger, *Ber.*, **89**, 2738 (1956). Molecular models reveal no significant differences in *exo*- and *endo*-faces of the two systems.

[10] The product of intramolecular *trans* addition was considered to be strained prohibitively.

[11] For a recent review, see O. Jeger, K. Schaffner, and H. Wehrli, *Pure Appl. Chem.*, **9**, 555 (1964).

[12] V. F. Kucherov and L. I. Ivanova, *Dokl. Akad. Nauk SSSR*, **131**, 1077 (1960); V. F. Kucherov, T. A. Severena, L. N. Ivanove, G. A. Cogan, and B. A. Rudenko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **8**, 1428 (1963).

[13] No significant amount of acidic material could be detected in these photolyses. It was anticipated that there would be some differences in the ratio of ketene/aldehyde depending on starting geometry.

[14] Y. Shigemitsu, Y. Odaira, and S. Tsutsumi, *Tetrahedron Letters*, No. 1, 55 (1967); D. Scharf and F. Korte, *ibid.*, 821 (1963); D. R. Arnold, R. L. Hinman, and A. H. Glick, *ibid.*, 1425 (1964).

[15] Radical additions to norbornenes frequently proceed *via* substantial *endo* attack: H. Kwart and L. L. Nyce, *J. Am. Chem. Soc.*, **86**, 2601 (1964) and N. A. LeBel, P. D. Beirne, E. V. Karger, J. C. Powers, and P. M. Subramanian, *ibid.*, **85**, 3199 (1963).

[16] D. R. Arnold, D. J. Trecker, and E. B. Whipple, *ibid.*, **87**, 2596 (1965).

[17] H. Morrison, *ibid.*, **87**, 932 (1965). "Vertical" triplet transfer seems unlikely on energetic grounds since E_T of simple aldehydes is probably less than 68.5 kcal/mole [J. D. Borman, J. H. Stanley, W. V. Sherman, and S. G. Cohen, *ibid.*, **85**, 4010 (1963)]. Sensitizers with less than E_T 71.6 kcal/mole do not transfer efficiently to norbornene.[14]

0.01 in. (i.d.) × 150 ft (Castorwax, Apiezon L, and Ucon 50-HB-2000). Melting points were determined on a Mel-Temp apparatus and are uncorrected.

3-Keto-*endo*-tricyclo[5.2.1.0^{2,6}]decane (2) was prepared by catalytic reduction of **4** and had mp 102–102.5° (lit.[4,18] mp 99–101°).

3-Keto-*exo*-tricyclo[5.2.1.0^{2,6}]decane (1) was prepared by catalytic reduction of **3** and had bp 54° (0.3 mm), lit.[19] bp 104–106° (11 mm).

Photolyses of 1 and 2.—A solution of 3.25 g of **2** in a mixture of 500 ml of dioxane and 100 ml of water was purged with nitrogen for 1 hr and irradiated under nitrogen with a 450-w Hanovia immersion lamp (Pyrex filter). The course of the reaction was followed by gas chromatography (Carbowax, 100°). A gradual buildup of **5** was observed. Subsequently, **6** began to appear. After 4 days, *ca.* 95% of the starting ketone had disappeared and a 2:1 mixture of **5–6** was present. On prolonged irradiation, the peak due to **5** diminished until it all but disappeared.

The solution was concentrated to 50 ml followed by addition of 200 ml of water. The resulting solution was made basic to litmus with sodium hydroxide and the neutral products were extracted into ether. Distillation of the extracts gave 1 g of material, bp 53–62° (0.45 mm) and 1 g of residue. The base-soluble material (0.38 g) was recovered by acidification of the aqueous solutions followed by ether extraction. Treatment of the extracts with ethereal diazomethane produced no noticeable nitrogen evolution and no significant amounts of esters could be detected by gas chromatography of the resulting ether solutions. Preparative gas chromatography (15-ft Carbowax, 140°) served to isolate the neutral volatile components.

The major component was assigned structure **5** on the basis of the following data. The infrared spectrum showed carbonyl absorption at 5.77 and an aldehyde band at 3.68 μ. Double-bond absorptions appeared at 6.15 and 11.53 μ. The nmr spectrum showed one proton at τ 0.34, one proton at 4.48 as a broad peak, a broad doublet (1 H) at 7.25, a broad singlet (4 H) at 7.57, and complex absorption (6 H) centered at 8.6.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.78; H, 9.30.

The minor photoproduct showed a strong absorption at 10.06 μ in the infrared spectrum and no other distinctive bands other than methylenic absorptions. The nmr spectrum in benzene showed two multiplets of equal area at τ 5.06 (doublet, J = 4.5 cps) and 5.24. Very complex absorption appeared at high fields, the total area of which was closer to 13 than 12. The source of this error was probably instrumental, since the compound appeared pure by gas chromatography on all capillary columns.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.68; H, 9.65.

A similar photolysis of 0.5 g of the *exo* ketone **1** in 100 ml of dioxane was carried out in a Rayonet reactor[20] using the light from the 3500 A sources. Within 13 hr enough **5** was formed for identification purposes (infrared). The oxetane **6** was present also as shown by comparative retention times.

Reduction of 6 with Lithium Aluminum Hydride.—A stirred mixture of 0.1 g of oxetane **6** and 0.15 g of lithium aluminum hydride in 15 ml of dry benzene was heated at reflux for 4 days. The salts were hydrolyzed with water and the precipitate was washed thoroughly with ether. After concentration of the extracts, a sample of the alcohol (only product) was collected by gas chromatography. The infrared and nmr spectra of this material were superimposable on those of the sample of **8** prepared below.

3,3-Trimethylenenorcamphor (9).—A solution of 22 g (0.20 mole) of norcamphor in 400 ml of dry ether was added to a stirred suspension of 23 g (0.6 mole) of sodium amide in 600 ml of ether over a 3.5 hour period. A nitrogen atmosphere was maintained at all times. After an additional hour, the mixture was poured onto 408 g (2 moles) of 1,3-dibromopropane and stirred for 2 days. The resulting solution was filtered and the precipitate was washed with ether. Evaporation of the combined solvents yielded 4 g of a liquid, bp 57° (8 mm). Gas chromatography (Carbowax, 130°) of the distillate indicated the presence of three components in roughly equal proportions. The product was dissolved in 100 ml of pentane and treated with aqueous potassium permanganate solution until no further discoloration of the permanganate was observed. The resulting mixture was filtered and the precipitate was washed with ethanol and pentane. The ethanol washings were added to the aqueous layer and the solution was extracted with pentane. The combined pentane extracts were washed with water and dried over magnesium sulfate. Evaporation of the pentane yielded 1 g of the ketone **9** which was homogeneous on gas chromatography.

Anal. Calcd for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.16; H, 9.29.

The infrared spectrum displayed bands at 5.78 (vs), 6.93, 7.60, 7.76, 9.10, 9.86, 10.70, 11.01 and 13.25 μ. The nmr spectrum showed a broad singlet at τ 7.53 (2 H) and complex absorption (12 H) centered at 8.3.

The *p*-nitrophenylhydrazone was crystallized from ethanol-water, mp 157.5–158.5°.

Anal. Calcd for $C_{16}H_{19}N_3O_2$: C, 67.35; H, 6.71; N, 14.73. Found: C, 67.17; H, 6.73; N, 14.94.

The **2,4-dinitrophenylhydrazone** melted at 160.6–161.5° after crystallization from ethanol-water.

Anal. Calcd for $C_{16}H_{18}N_4O_4$: C, 58.17; H, 5.49; N, 16.96. Found: C, 57.87; H, 5.55; N, 17.17.

Lithium Aluminum Hydride Reduction of 9.—Reduction was effected by treatment of 0.7 g (4.6 mmoles) of ketone **9** in 50 ml of ether with 0.1 g of lithium aluminum hydride. After stirring for 1 hr at 25°, the mixture was carefully hydrolyzed. The salts were removed by filtration and were washed with ether. The combined washings were concentrated and analyzed by gas chromatography (Carbowax, 170°). The major component (95%) had a retention time identical with that of the product obtained from the oxetane. The minor product was assumed to be the *exo* alcohol and was not isolated.

The infrared spectrum of alcohol **8** had bands at 3.0, 9.13, 9.45, 9.75, 12.55 (w), and 13.28 (w) μ. The nmr spectrum showed a sharp doublet (J = 4.5 cps) at τ 6.33 (1 H), a sharp singlet (1 H) at 7.42 and complex absorption (14 H) centered at 8.4.

Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.99; H, 10.72.

Epoxidation of 4.—A solution of 20 g (0.14 mole) of the unsaturated ketone **4** in 100 ml of methanol was treated with a solution of 40 ml of 15% hydrogen peroxide in 36 ml of 2 *N* sodium hydroxide solution. The temperature was maintained below 30° during the addition. Solvents were removed by evaporation under vacuum and the residue, 18.1 g (82%), was crystallized from ether–hexane. The melting point rose from 142–144° to 144–145° during purification. Gas chromatography (Carbowax, 150°) indicated one component.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.20; H, 7.32. Found: C, 73.19; H, 7.32.

The infrared spectrum showed bands at 5.80 (vs), 6.82, 6.94, 7.38, 7.77, 8.52, 9.98, 11.25, 11.80, and 12.10 (S) μ.

Photolysis of 11.—A solution of 3 g of **11** in 600 ml of cyclohexane was irradiated under nitrogen with a 450-w Hanovia lamp (Pyrex filter). After 21 hr 2 g of a white solid had precipitated which was purified by sublimation at 140° (0.1 mm), mp 170–171° (lit.[12] mp 166–166.5°).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.22; H, 7.55.

The ultraviolet spectrum in methanol showed a maximum absorption at 254 mμ (ϵ 12,000), lit.[12] λ_{max} 251 mμ (ϵ 13,200). The infrared spectrum showed a broad hydroxyl peak at 3.9 a strong peak at 6.42 and a medium intensity band at 6.12 μ (lit.[12] 6.47 and 6.16 μ). Four broad singlets appeared at τ 8.63 (4 H), 8.38 (2 H), 7.40 (2 H), and 7.04 (2 H). Sharp singlets were observed at τ 4.74 (1 H) and −2.95 (1 H).

The monobromide melted at 226.5–228° (lit.[12] mp 226–228°).

Acetylation of 13.—A solution of 1 g of the enol **13** in 5 ml of acetic anhydride was heated at 110° for 14 hr. Evaporation of the solution *in vacuo* yielded a residue which was crystallized from petroleum ether (30–60°). A 60% yield (0.75 g) of **14** was obtained, mp 78–79°.

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.16; H, 6.82.

Strong infrared absorptions were recorded at 5.57, 5.85, and 6.25 μ.

Reduction of 14.—A solution of 0.5 g of enol acetate **14** in 10 ml of absolute ethanol was stirred in the presence of 1 g of Raney nickel under a hydrogen atmosphere. Distillation of the

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(18) J. Pirsch, *Ber.* **67**, 1115 (1934).

(19) M. M. Donaldson, Ph.D. Thesis, Princeton University, 1958.

(20) S. N. E. Ultraviolet Co., Middletown, Conn.

filtered solution yielded a liquid which on gas chromatography (Carbowax, 155°) showed three components. The major product (*ca.* 55%) was isolated and shown to have an infrared and nmr spectrum identical with those of 3-keto-*endo*-tricyclo-$[5.2.1.0^{2,6}]$decane (**2**).

Registry No.—**5**, 13970-41-7; **6**, 13970-42-8; **8**, 13865-12-8; **9**, 13865-13-9; *p*-nitrophenylhydrozone of **9**, 13865-14-0; 2,4-dinitrophenylhydrazone of **9**, 13865-15-1; **11**, 13865-16-2; **14**, 13970-43-9.

Acknowledgments.—We are grateful to the Petroleum Research Fund (No. 1676-A1) and the Research Council, Rutgers, The State University, for generous financial support.

The Mass Spectra of Small-Ring Heterocycles. I. Some 1-Alkyl-2-phenyl-3-aroylazetidines

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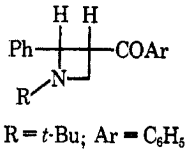
Received March 20, 1967

The mass spectra of nine 1-alkyl-2-phenyl-3-aroylazetidines (I–IX) are described, and a method for distinguishing between *cis*- and *trans*-aroylazetidines is presented and discussed. An unusual, simple fission of the 1-alkyl–nitrogen bond is also described. The preparation and characterization of three new azetidines (VII, VIII and IX) are described.

No reference to the mass spectra of azetidines has appeared in the literature. In conjunction with other studies being carried out in this laboratory[3] and in an attempt to establish a method for distinguishing between the *cis* and *trans* isomers by mass spectroscopy, the mass spectra of the following 1-alkyl-2-phenyl-3-aroylazetidines were determined: *trans*-1-*t*-butyl-2-phenyl-3-benzoylazetidine (I; series **1**; Figure 1), *trans*-1-*t*-butyl-2-phenyl-3-benzoyl-3-deuterioazetidine (II; series **1**; Figure 2), *cis*-1-*t*-butyl-2-phenyl-3-benzoylazetidine (III; series **1**; Figure 3), *trans*-1-*t*-butyl-2-phenyl-3-*p*-phenylbenzoylazetidine (IV; series **2**; Figure 4), *trans*-1-*t*-butyl-2-phenyl-3-*p*-phenylbenzoyl-3-deuterioazetidine (V; series **2**; Figure 5), *cis*-1-*t*-butyl-2-phenyl-3-*p*-phenylbenzoylazetidine (VI; series **2**; Figure 6), *trans*-1-cyclohexyl-2-phenyl-3-*p*-phenylbenzoylazetidine (VII; series **3**; Figure 7), *trans*-1-cyclohexyl-2-phenyl-3-*p*-phenylbenzoyl-3-deuterioazetidine (VIII; series **3**; Figure 8), and *cis*-1-cyclohexyl-2-phenyl-3-*p*-phenylbenzoylazetidine (IX; series **3**; Figure 9).



series 1, $R = t\text{-Bu}$; $Ar = C_6H_5$
series 2, $R = t\text{-Bu}$; $Ar = p\text{-}C_6H_5C_6H_4$
series 3, $R = C_6H_{11}$; $Ar = p\text{-}C_6H_5C_6H_4$

It might be expected that the predominant process occurring when the aroylazetidines are subjected to electron impact would be the removal of one of the nonbonding electrons from one of the heteroatoms. It is generally accepted that nitrogen is capable of stabilizing a positive charge more readily than oxygen[4] and, in fact, in the somewhat similar case of tropinone,[5] where the nitrogen and carbonyl functions are also separated by three bonds, the entire fragmentation pattern may be rationalized on the basis of the removal of an electron from nitrogen. However, in the present case, the carbonyl group is adjacent to an aromatic system and a positive charge on oxygen would be stabilized by resonance interaction with the aromatic ring. Therefore, although electron-shift mechanisms can be drawn to account for the origin of all major fragments by removal of an electron from nitrogen, the removal of a nonbonding electron from oxygen is undoubtably an important process for these azetidines, especially in the formation of the fragment which allows *cis* and *trans* isomers to be easily distinguished.

Previous studies of *cis* and *trans* isomers have generally been more or less successful in establishing distinct fragmentation patterns for each isomer[6] based on relative differences in intensities of certain key fragments. This technique requires that the spectra of both *cis* and *trans* isomers be available for comparison.

In the 2-phenyl-3-aroylazetidines it is possible to distinguish between *cis* and *trans* isomers by the presence or absence of specific fragments in the mass spectrum. Although pairs of isomers of known configuration were available for comparison in the present study, it should be possible to apply these results to future cases in similar and related systems where both isomers are not available or are of unknown configuration. This possibility is being investigated in other systems.

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[2] Texaco Fellow in Chemistry, 1966–1967.

[3] (a) E. Doomes and N. H. Cromwell, *Tetrahedron Letters*, 4037 (1966). (b) J.-L. Imbach, E. Doomes, R. P. Rebman, and N. H. Cromwell, *J. Org. Chem.*, **32**, 78 (1967).

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