The Photochemistry of Bicyclo[6.1.0]nonan-3-one, Bicyclo[6.1.0]nonan-4-one, and Cyclooctanone

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Irradiation of bicyclo[6.1.0]nonan-3-one (**1**) in *tert*-butyl alcohol gave 2-allylcyclohexanone (**2**), 3-vinylcycloheptanone (**3**), and *tert*-butyl non-8-enoate (**4**). When irradiated in ether, the ketone **1** gave bicyclo[6.1.0]nonan-3-ol (**5**) and the isomeric 3-(1-ethoxyethyl)bicyclo[6.1.0]nonan-3-ol (**6**). In ether, bicyclo[6.1.0]nonan-4-one (**7**) gave bicyclo[6.1.0]nonan-4-ol (**8**) and the isomeric 4-(1-ethoxyethyl)bicyclo[6.1.0]nonan-4-ol (**9**). In *tert*-butyl alcohol, the ketone **7** gave mixtures of aldehydes **10** and **11** and *tert*-butyl esters **12** and **13**. Irradiation of cyclooctanone (**14**) in *tert*-butyl alcohol gave the isomeric 2-(3-buten-1-yl)cyclobutanol (**15**) and *tert*-butyl octanoate (**16**). In ether, the ketone **14** gave cyclooctanol (**17**) and 1-(1-ethoxyethyl)cyclooctanol (**18**).

Cyclopropyl groups have been known to affect the course of a photoreaction. Most attention has centered on cyclopropyl rings α to or conjugated with a carbonyl group. Many of these studies have indicated that the cyclopropyl bond which best overlaps with the π lobes of the carbonyl group undergoes a rapid photoreaction in a highly specific manner.[1,2]

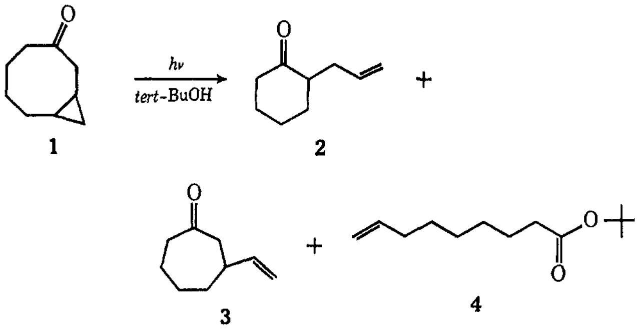
In ring compounds of C_5 and C_6 the conformation is rigid, permitting overlap of only one of the cyclopropyl bonds with the carbonyl group. In the case of the bicyclo[6.1.0]nonan-2-one, it has been shown by Paquette[3] that the ring has enough flexibility to permit the overlap of the two adjacent cyclopropyl bonds with the π lobes of the carbonyl group.

While there has been considerable attention cast upon the photochemistry of conjugated cyclopropyl ketones, there is little information available on the effect of a cyclopropane ring that is not conjugated with a carbonyl group. Wiberg[4] has noted that there is an interaction between the cyclopropane ring and the carbonyl group in both bicyclo[6.1.0]nonane-2-one and bicyclo[6.1.0]nonan-3-one, but none was observed in bicyclo[6.1.0]nonan-4-one. In the photochemistry of 3- and 4-cyclooctenone, the double bond has been shown to have a very distinct effect on the course of the reaction[5,6] leading to ring-contracted products. It was therefore of interest to study the photochemistry of a ketone with a nonconjugated cyclopropane ring. We wish to report here such a study on bicyclo[6.1.0]nonan-3-one and bicyclo[6.1.0]nonan-4-one. As a comparison, we also studied the photochemistry of cyclooctanone. Past evidence indicates that the cyclopropane ring not conjugated with the carbonyl group can influence the course of the reaction.[7,8]

The photolyses were carried out in an immersion well apparatus using a 550-W Hanovia medium-pressure mercury vapor lamp using a Corex filter. The photolyses were conducted for 3 hr in dilute solutions (less than 1%).

Bicyclo[6.1.0]nonan-3-one (**1**) was prepared by the oxidation of bicyclo[6.1.0]nonan-3-ol (**5**) which was obtained from 3-cyclooctenol by the Simmons-Smith reaction.

After 3 hr of irradiation of **1** in *tert*-butyl alcohol, all of the starting ketone was consumed and the photoproduct[9] gave four major peaks on the gas chromatograph in a ratio of 46:15:23:14. They were 2-allylcyclohexanone (**2**), 3-vinylcycloheptanone (**3**), and *tert*-butyl non-8-enoate (**4**). The fourth component appeared to be a mixture in which an aldehyde appeared to be the major product.



2-Allylcyclohexanone (**2**) was identified by comparison with an authentic sample, prepared by alkylation of the pyrrolidine enamine of cyclohexanone with allyl bromide.

The nmr spectrum of **3** showed absorption for a terminal vinyl group. It also showed a sharp 4-proton peak at τ 7.6. The structure of this compound was determined by hydrogenating the photolysate of **1** and isolating 3-ethylcycloheptanone, which was identified by comparison with an authentic sample prepared by treating 2-cycloheptenone with ethylmagnesium iodide in the presence of a catalytic amount of cuprous chloride.

The nmr spectrum of **4** also showed absorption for a terminal vinyl group. The ir spectrum showed an ester absorption at 1730 cm^{-1} and peaks at 1400 and 1375 cm^{-1} accounting for a *tert*-butyl group. The structure of **4** was determined by isolating it by glpc and hydrogenating it to the *tert*-butyl nonanoate, which was also independently synthesized from nonanoic acid and isobutylene.

An attractive rationale for the mechanism of this reaction would be the formation of the cyclopropyl carbinyl radical by α cleavage, followed by rearrange-

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[1] L. D. Hess and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 1973 (1967).

[2] L. D. Hess, J. L. Jacobson, K. Schaffner, and J. N. Pitts, Jr., *ibid.*, **89**, 3684 (1967).

[3] L. A. Paquette and R. F. Eizember, *ibid.*, **91**, 7108 (1969).

[4] K. B. Wiberg and A. de Meijere, *Tetrahedron Lett.*, 59 (1969).

[5] J. K. Crandall, J. P. Arrington, and R. J. Watkins, *Chem. Commun.*, 1052 (1967).

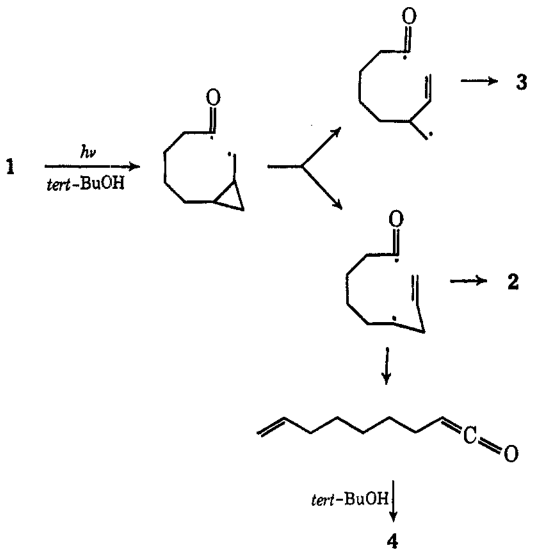
[6] (a) J. K. Crandall, J. P. Arrington, and J. Hen, *J. Amer. Chem. Soc.*, **89**, 6208 (1967); (b) L. A. Paquette and R. F. Eizember, *ibid.*, **89**, 6205 (1967).

[7] R. G. Carlson and E. L. Biersmith, *Chem. Commun.*, 1049 (1969).

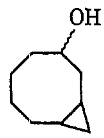
[8] D. C. Heckert and P. J. Kropp, *J. Amer. Chem. Soc.*, **90**, 4911 (1968).

[9] We have learned that Professor Crandall has also studied the photochemistry of this compound. We thank Professor Crandall for informing us of his results prior to publication.

ments to the homoallylic radicals leading to the products, as shown below.



In ether, the photolysis of **1** took a somewhat different course. Photoreduction competed significantly with ring opening. The products were **2**, **3**, bicyclo[6.1.0]nonan-3-ol (**5**), and the isomeric 3-(1-ethoxyethyl)bicyclo[6.1.0]nonan-3-ol (**6**) in a ratio of 32:10:32:26.



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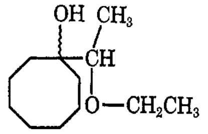

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The ir spectrum as well as the retention time on glpc of **5** was identical with that of the reduction product of **1** with either sodium in alcohol or lithium aluminum hydride. Glpc analysis on several polar and nonpolar columns did not separate **5** into the isomeric alcohols, and the stereochemistry of **5** was not assigned.

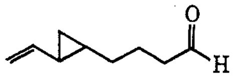
The mass spectrum of **6** showed a parent peak at m/e 212 and strong peaks at m/e 139 and 73 indicating the loss of the ether group. The ir spectrum showed a peak for a hydroxyl group, and the nmr spectrum confirmed the presence of a cyclopropyl proton.

Bicyclo[6.1.0]nonan-4-one (**7**) was synthesized by oxidation of 4-cyclooctenol to 4-cyclooctenone, followed by the Simmons–Smith reaction. This route was found to be superior to the alternative route of the Simmons–Smith reaction on 4-cyclooctenol, followed by oxidation to **7**.

The irradiation of **7** in ether yielded a mixture of three components in a ratio of 8:32:60. The first component was the ketone **7** and the second was identified as bicyclo[6.1.0]nonan-4-ol (**8**). The product had the same ir spectrum as the product obtained from the oxymercuration of bicyclo[6.1.0]non-4-ene. The stereochemistry of **8** was not determined.

The third component was assigned the structure of 4-(1-ethoxyethyl)bicyclo[6.1.0]nonan-4-ol (**9**). The mass spectrum of this compound showed apparent peak at m/e 212 and strong peaks at m/e 138 and 73 indicating the loss of the ether group. The infrared spectrum showed bands for a hydroxyl group and an ether group, and the nmr spectrum indicated the presence of a cyclopropane proton.

In *tert*-butyl alcohol, the ketone **7** gave a mixture of three components in a ratio of 22:15:63. The presence of an aldehyde group in the first component was indicated by the ir and nmr spectra. The nmr spectrum also indicated that a terminal vinyl group was present. A cyclopropyl group was also indicated in the nmr at τ 10.1. On the basis of this evidence, structures **10** and **11** were tentatively assigned to this component.



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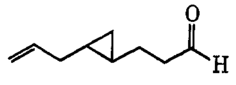

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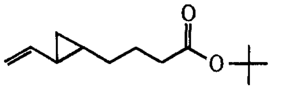

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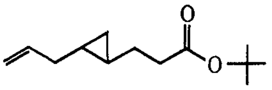

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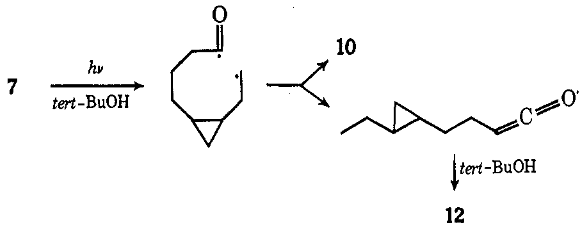
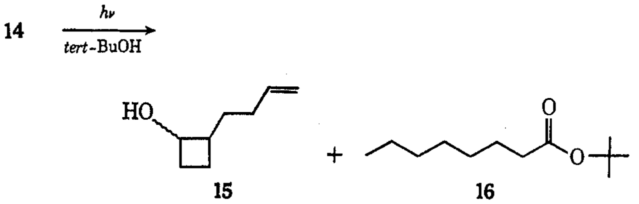
The second component was the ketone **7** while the third was a mixture of *tert*-butyl esters. The ir spectrum showed a carbonyl absorption at 1735 cm^{-1}, and bands at 1400 and 1365 cm^{-1}, indicating the presence of a *tert*-butyl group. The cyclopropyl absorption was also indicated in the nmr spectrum at τ 10.15. Based on this evidence, the isomeric structures of **12** and **13** were assigned to this component.

A plausible mechanism for this reaction is primary α cleavage followed by hydrogen abstraction to form either the aldehydes or the ketenes. The ketenes then can react with the *tert*-butyl alcohol to form the products.



For purposes of comparison, cyclooctanone (**14**) was photolyzed.[10] Irradiation of **14** in *tert*-butyl alcohol yielded a mixture which contained three components in a ratio of 15:79:6. The structure of the first component was assigned as 2-(3-buten-1-yl)cyclobutanol (**15**). The nmr spectrum of this component indicated a terminal vinyl group and two different protons α to the hydroxyl group each integrating to $^{1}/_{2}$ of a proton. Confirmation of this structure was made by oxidizing the crude photolysate and isolating the cyclobutanone formed, which had an infrared absorption for the carbonyl group at 1775 cm^{-1}.



The second component of the mixture was cyclooctanone and the third product, which showed an ester absorption in the ir spectrum, was shown to be *tert*-

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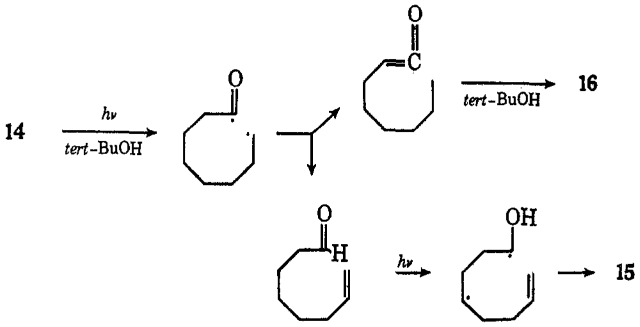
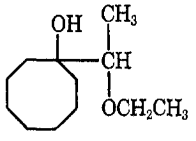
[10] N. C. Yang, Abstracts, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, 1960, No. O-53.

butyl octanoate (**16**) by independent synthesis from octanoic acid and isobutylene.

The products **15** and **16** probably arise from α cleavage followed by hydrogen atom transfer to form either the aldehyde or the ketene. The aldehyde then rearranges to the alcohol by a type II rearrangement, while the ketene reacts with *tert*-butyl alcohol to give the ester.



The photolysis of cyclooctanone in ether also gave a mixture of three components, but in a ratio of 6:48:46. They were identified as **14** and cyclooctanol (**17**) by their retention times. The structure of the third component was assigned as 1-(1-ethoxyethyl)cyclooctanol (**18**) based on carbon-hydrogen analysis and spectral data. The nmr showed a 3-proton absorption at τ 6.2-7.0 (protons α to the ethereal oxygen) and a 6-proton absorption at τ 8.9 (two methyl groups). There was also a peak at τ 8.45 which integrated for 14 protons. The ir showed a band at 3570 cm^{-1}, suggesting a *tert*-hydroxyl group.



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In cyclohexane, the photolysis of **14** gave cyclooctanol (38%) and several high-molecular-weight hydrocarbons (52%) in addition to **14** (9%). In our hands, in the solvents we used, we were unable to find bicyclo[3.3.0]octan-1-ol previously reported by Yang.[10] However, the exact experimental conditions under which this bicyclic alcohol was formed was not available in the literature.[10]

The photochemistry of ketones **1** and **7** and cyclooctanone are remarkably solvent dependent. In polar, nonhydrogen donating solvents, such as *tert*-butyl alcohol, α cleavage is the primary mode of photoreaction. In less polar solvents where hydrogen donation is possible, such as ether, photoreduction becomes the predominant pathway.

How the cyclopropyl group affects the reactivity of these compounds can be seen by comparing the photochemistry of **1** and **7** to that of cyclooctanone. The ketone **1** splits open quickly in *tert*-butyl alcohol to yield ring-contracted products and esters. The ketone **1** in this case is completely consumed within 15 min. In a similar manner, the ketone **7** splits open rapidly in *tert*-butyl alcohol, but 15% of it is left unchanged at the end of 3 hr. In contrast, cyclooctanone is consumed more slowly and 79% of the ketone is left at the end of 3 hr. Thus the cyclopropyl group must have a definite influence on the reactivity of the two bicyclic ketones.

It is significant that the components of the products from the photolysis of the ketone **7** maintain the cyclopropane ring, whereas those from the ketone **1** do not.

In ether, the results are quite different. The ketone **1** splits open rapidly again and also shows photoreduced products. Thus, the cyclopropane ring must still have considerable influence on the reactivity of this molecule. In the ketone **7** and cyclooctanone, only photoreduced products are observed. Here the cyclopropane ring in **7** does not seem to influence the reactivity of this ketone.

Two generalizations seem to come from the photochemistry of these bicyclic ketones. The first is that the solvent seems to have a distinct effect on the course of the reaction. The second is that the proximity of the cyclopropyl group with respect to the carbonyl group plays an important role in the formation of these products.

Experimental Section[11]

Bicyclo[6.1.0]nonan-3-ol (5).[12]—To a rapidly stirring solution of 46.8 g of the zinc-copper couple[13] in 150 ml of anhydrous ether was added a small crystal of iodine. When the brown color was discharged, a mixture of 3-cyclooctenol[14] (25.6 g, 0.203 mol) and methylene iodide (69 g, 0.257 mol) was added dropwise. When all the alcohol was added, the mixture was refluxed for 72 hr.[15] The mixture was then cooled and the solids were removed by filtration. The solids were washed with ether and the combined ether extracts were washed with two 50-ml portions of saturated ammonium chloride solution and two 50-ml portions of saturated sodium carbonate solution, dried ($MgSO_4$), and concentrated. Glpc analysis indicated that the product consisted of an equal amount of 3-cyclooctenol and **5**. Fractional distillation gave 7.6 g of 3-cyclooctenol, bp 108-112° (20 mm), and 11.4 g (40%) of **5**, bp 128-132° (20 mm): ir (CCl_4) 3350, 3060, 1110, 1050 cm^{-1}; nmr (CCl_4) τ 6.2 (m, 1 H), 7.6-9.7 (m, 14 H), 10.2 (m, 1 H).

Anal. Calcd for $C_9H_{16}O_1$: C, 77.08; H, 11.50. Found: C, 77.16; H, 11.32.

Bicyclo[6.1.0]nonan-3-one (1).—To 4.0 g (0.0285 mol) of bicyclo[6.1.0]nonan-3-ol (**5**) in 100 ml of acetone was added dropwise a chromic acid solution prepared from 3.7 g of chromic anhydride, 3.3 ml of concentrated sulfuric acid, and 13 ml of water. The temperature of the reaction flask was not allowed to rise above 35° and the addition was continued until the orange color persisted for 1 min. The residual green salts were removed by filtration and washed with two 25-ml portions of acetone. The combined acetone extract was stirred with 5 g of solid $NaHCO_3$ for 0.5 hr. The solids were removed and the acetone layer was concentrated by distillation over a steam bath until 90 ml of acetone was collected. The residual water layer was extracted with three 50-ml portions of ether and the ether layer was dried ($MgSO_4$) and concentrated. Distillation of the crude product afforded 2.5 g (63%) of **1**, bp 44-48° (0.3 mm): ir (CCl_4) 3060, 1700 cm^{-1}; nmr (CCl_4) τ 6.95-8.9 (broad, 13 H), 9.85 (m, 1 H).

Irradiation of 1 in Ether.—A solution of 0.73 g (0.0053 mol) of **1**[16] in 250 ml of anhydrous ether was irradiated for 3 hr with a

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[11] Nmr spectra were determined on a Varian A-60 spectrophotometer; chemical shifts are reported in τ values in parts per million using tetramethylsilane (TMS) as an internal standard. Infrared spectra were recorded on a Perkin-Elmer Model 257 grating infrared spectrophotometer. Gas chromatography was performed on an F & M Model 720 thermal conductivity gas chromatograph using 2- or 4-ft columns containing 20% neopentyl glycol succinate (NGS) on Chromosorb W, 20% silicone grease on Chromosorb W, and 30% silicone fluid F50 on Chromosorb P. Boiling points are uncorrected.

[12] A. C. Cope and G. L. Woo, *J. Amer. Chem. Soc.*, **85**, 3601 (1963).

[13] R. D. Smith and H. E. Simmons, *Org. Syn.*, **41**, 72 (1961).

[14] (a) A. C. Cope and P. E. Peterson, *J. Amer. Chem. Soc.*, **81**, 1643 (1959); (b) J. K. Crandall, D. B. Banks, R. A. Colyer, R. J. Watkins, and J. P. Arrington, *J. Org. Chem.*, **33**, 423 (1968).

[15] The reaction can be very exothermic in the first 2 hr.

[16] All compounds which were photolyzed were purified by distillation followed by isolation by glpc.

550-W Hanovia mercury vapor lamp in an immersion well apparatus fitted with a Corex filter.

Gas chromatographic analysis (silicon grease, 140°) of the photolysis product indicated the presence of four products: 2-allylcyclohexanone (**2**, 32%), 3-vinylcycloheptanone (**3**, 10%), bicyclo[6.1.0]nonan-3-ol (**5**, 26%), and the isomeric 3-(1-ethoxyethyl)bicyclo[6.1.0]nonan-3-ol (**6**, 26%).

A sample of **2** was isolated by glpc and identified by comparison of its glpc retention time and nmr and infrared spectra with those of an authentic sample prepared by the method of Stork.[17] A sample of **2** isolated by glpc exhibited the following spectral properties: ir (CCl_4) 3090, 2940, 2870, 1715, 1645, 1000, 922 cm^{-1}; nmr (CCl_4) τ 4.5 (m, 1 H), 4.9 (m, 1 H), 5.2 (m, 1 H), 7.5–8.9 (m, 11 H).

A sample of **3**, also isolated by glpc, exhibited the following spectral properties: ir (CCl_4), 3080, 1705, 1645, 1000, 922 cm^{-1}; nmr (CCl_4) τ 4.05–4.8 (m, 1 H), 5.0 (d, 1 H), 5.2 (m, 1 H), 7.5–9.1 (11 H).

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.20; H, 9.92.

A sample of **6** had the following spectral properties: ir (CCl_4) 3580, 3080, 2990, 2930, 1100 cm^{-1}; nmr (CCl_4) τ 6.3–6.9 (3, m), 7.6–9.5 (20), 10.3 (1, m); mass spectrum (70 eV) *m/e* 212, 139, 73.

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.61; H, 11.22.

Irradiation of 1 in *tert*-Butyl Alcohol.—A solution of 1.0 g of **1** in 250 ml of freshly distilled *tert*-butyl alcohol was irradiated through a Corex filter for 3 hr. Removal of the *tert*-butyl alcohol by distillation through a Vigreux column afforded 0.97 g of a colorless liquid. Gas chromatographic analysis (silicone grease, 140°) indicated the presence of **2** (46%), **3** (15%), and *tert*-butyl non-8-enoate (**4**, 23%). In addition, there was a component (14%) which was an unresolvable mixture of compounds. Its infrared and nmr spectra indicated the presence of an aldehyde. A sample of **4**, isolated by glpc, exhibited the following spectral properties: ir (CCl_4) 3080, 1735, 1400, 1375, 1160, 1000, 920 cm^{-1}; nmr (CCl_4) τ 4.1–4.6 (m, 1 H), 4.75–4.95 (m, 1 H), 5.25 (m, 1 H), 7.8 (m, 4 H), 8.65 (m, 17 H).

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.50; H, 11.24.

Hydrogenation of the Photoproduct of 1.—A solution of 0.410 g of the photoproduct of **1** in *tert*-butyl alcohol in 100 ml of ether was hydrogenated at 40 lb of pressure over 5% palladium on charcoal for 24 hr. Isolation of the crude product yielded 0.305 g (74.5%).

Glpc analysis (silicone oil, 160°) indicated the presence of nine peaks. 2-Propylcyclohexanone (**19**, 43%), isolated by glpc, was identified by comparison of the ir and nmr spectra with those with an authentic sample obtained by hydrogenating 2-allylcyclohexanone. 3-Ethylcycloheptanone (**20**, 12%), isolated by glpc, was identified by comparison of the ir and nmr spectra with those of an authentic sample prepared as described below. Nonanoic acid (**21**, 8%) and *tert*-butyl nonanoate (**22**, 8%) were not separated on the silicone column, but they could be separated on the NGS column. Samples of **21** and **22** were first isolated on the silicone oil column as one peak and further isolated on the NGS column and identified by comparison of their infrared spectrum with those of authentic samples. There were five other components corresponding to 21% which were not identified.

3-Ethylcycloheptanone (20).[18]—To a solution of ethylmagnesium iodide prepared from 0.8 g of magnesium turnings and ethyl iodide (2.12 g, 0.9136 mol) in 50 ml of dry ether was added 0.1 g of cuprous chloride. The mixture was stirred for 5 min. The solution was cooled to 0° and a solution of 1.0 g (0.0091 mol) of 2-cycloheptenone[19] in 10 ml of ether was added slowly. The mixture was stirred overnight at room temperature and poured into ice, and 2 ml of 20% H_2SO_4 was added. The mixture was extracted with three 25-ml portions of ether and the combined ether layers were washed with 25 ml of 10% sodium thiosulfate solution, dried ($MgSO_4$), and concentrated. Glpc analysis (NGS, 140°) of the crude material indicated that it was homogeneous. The crude product was distilled yielding 0.4 g (40%) of **20**, bp 75–77° (20 mm) [lit.[18] 122–125° (100 mm)]: ir (CCl_4) 2940, 2870, 1705, 1415, 1405, 1390, 1365, 1330, 1260 cm^{-1}; nmr (CCl_4) τ 7.45 (m, 4 H), 7.65–8.55 (broad, 9 H), and 8.9 (t, 3 H).

***tert*-Butyl Nonanoate (22).**—A solution of 10 g (0.064 mol) of nonanoic acid, 7 ml (*ca.* 0.127 mol) of isobutylene, 1 ml of concentrated H_2SO_4, and 75 ml of ether was placed in a pressure bottle and shaken overnight. The contents were then poured into an ice-cold mixture of 7 g of NaOH in 50 ml of water. The mixture was kept cold and stirred for 10 min. The ether layer was then washed with two 25-ml portions of water, dried ($MgSO_4$), and concentrated. The crude product was distilled yielding 5.4 g (39%) of **22**, bp 70–71° (0.4 mm): ir (CCl_4) 2940, 2870, 1735, 1400, 1375, 1150 cm^{-1}; nmr (CCl_4) τ 8.0 (m, 2 H), 8.8 (m, 21 H), 9.2 (t, 3 H).

Anal. Calcd for $C_{13}H_{26}O_2$: C, 72.84; H, 12.22. Found: C, 72.84; H, 12.05.

Reduction of 1 with Lithium Aluminum Hydride.—A solution of 0.2 g (0.0145 mol) of **1** and 0.1 g (0.00264 mol) of lithium aluminum hydride in 50 ml of ether was heated to reflux for 2 hr. At the end of this period, 2 ml of water was added and the mixture was dried ($MgSO_4$). The solids were removed and the ether layer was concentrated. Glpc analysis of the crude product indicated that it consisted of one major peak which had the same retention time as **5**. The ir spectrum of this product was also identical with that of **5**.

Reduction of 1 with Sodium in Ethanol.—A solution of 0.2 g (0.0014 mol) of the ketone **1**, 0.2 g (0.0087 g-atom) of sodium, and 25 ml of ethanol in 50 ml of toluene was refluxed for 2.5 hr, cooled, and washed with two 25-ml portions of 3% HCl. The toluene layer was dried ($MgSO_4$) and concentrated. Glpc analysis of the crude mixture indicated that one major peak was present which had the same retention time as **5**. The ir spectrum of this fraction was identical with that of **5**.

Irradiation of Cyclooctanone (14) in *tert*-Butyl Alcohol.—A solution of 2.2 g of cyclooctanone in 250 ml of ether was irradiated for 3-hr through a Corex filter. The *tert*-butyl alcohol solution was then concentrated. Glpc analysis of the crude photolysate indicated the presence of three products in a ratio of 15:79:6. The first component was assigned the structure of 2-(3-buten-1-yl)cyclobutanol (**15**) based on the ir and nmr spectra: ir (CCl_4) 3620, 3340, 3080, 1645, 1120, 1000, 920 cm^{-1}; nmr (CCl_4) τ 4.0–4.7 (m, 1 H), 4.8–5.3 (t, 2 H), 5.7 (m, $^1/_2$ H), 6.3 (m, $^1/_2$ H), 6.4 (s, 1), 7.6–8.4 (m, 9 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.13; H, 11.18. Found: C, 75.94; H, 10.87.

The second component was shown to be cyclooctanone (**14**) by comparison of the retention time on glpc and by comparison of the ir spectrum of the product isolated from chromatography with those of the authentic sample.

The third product was identified as *tert*-butyl octanoate (**16**) by comparison of its ir and nmr spectra with those of an authentic sample prepared as described below.

Irradiation of Cyclooctanone (14) in Ether.—A solution of 5 g of cyclooctanone in 250 ml of ether was irradiated for 3 hr through a Corex filter. The ether layer was concentrated. Glpc analysis of the crude product indicated the presence of three components in a ratio of 6:48:46. The first and second components were identified as cyclooctanone and cyclooctanol, respectively, by comparison of the retention times and ir spectra with those of authentic samples.

The structure of the third product was assigned as 1-(ethoxyethyl)cyclooctanol (**18**): ir (CCl_4) 3570, 2930, 1100 cm^{-1}; nmr (CCl_4) τ 6.2–6.9 (m, 3 H), 8.05 (s, 1 H), 8.15–8.65 (14 H), 8.7–9.1 (m, 6 H).

Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 72.16; H, 12.21.

***tert*-Butyl Octanoate (16).**—A solution of 10.0 g (0.069 mol) of octanoic acid, 2 ml of H_2SO_4, and 20 ml of isobutylene (*ca.* 0.364 mol) in 75 ml of ether was placed in a pressure bottle and shaken overnight. The mixture was then poured into an ice-cold solution of 7 g of NaOH in 50 ml of water and stirred for 10 min. The ether layer was separated and washed with two 25-ml portions of water, dried ($MgSO_4$), and concentrated. The product was distilled yielding 4.7 g (33.7%) of **16**, bp 55–57° (0.5 mm): ir (CCl_4) 2940, 1735, 1400, 1375, 1155 cm^{-1}; nmr (CCl_4) τ 7.8 (m, 2 H), 8.3–8.9 (m, 19 H), 9.0–9.3 (m, 3 H).

Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 71.90; H, 12.00.

Bicyclo[6.1.0]nonan-4-one (7).—To a mixture of 18 g of the zinc-copper couple in 100 ml of ether was added a crystal of iodine. When the brown color was discharged, a mixture of 31 g

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[17] G. Stork, A. Brizzolarra, H. Landesman, J. Szmuskovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

[18] T. Nozoe, T. Mukai, and S. Matsumoto, *Proc. Jap. Acad.*, **27**, 110 (1951).

[19] N. Heap and G. Whitham, *J. Chem. Soc. B*, 164 (1966).

(0.248 mol) of 4-cyclooctenone[19] and 73 g (0.27 mol) of methylene iodide was added in one portion. The mixture was refluxed for 2 days, after which glpc analysis of the ether solution indicated that the reaction had only gone to a small extent (*ca.* 30%). Another 18 g of the zinc–copper couple was added to the mixture and this was followed by another 73 g (0.27 mol) of methylene iodide. The mixture was then refluxed for another 2 days. The mixture was then filtered and the filtrate was washed with two 100-ml portions of a 5% HCl solution, two 100-ml portions of saturated Na_2CO_3 solution, and two 100-ml portions of water, dried ($MgSO_4$), and concentrated. The product was distilled, yielding 16.2 g (47%) of **7**, bp 97–100° (15 mm). Glpc analysis of the distilled product indicated that two products were present in a ratio of 16:84. The first product was 4-cyclooctenone, while the second was bicyclo[6.1.0]nonan-4-one (**7**): ir (CCl_4) 3075, 3000, 2940, 2870, 1705, 1355, 1345, 1170 cm^{-1}; nmr ($CDCl_3$) τ 7.4–8.7 (10 H), 9.3 (m, 3 H), 10.15 (m, 1 H).[4]

Irradiation of 7 in Ether.—A solution of 0.66 g of **7** in 250 ml of ether was irradiated for 3 hr through a Corex filter. At the end of this period, the ether layer was concentrated. Glpc analysis of the crude product indicated the presence of three products ratio of 8:32:60. The first product had the same retention time and ir spectrum as **7**. The second product was bicyclo[6.1.0]nonan-4-ol (**8**): ir (CCl_4) 3610, 3320, 3070, 3000, 2920, 2860, 1030 cm^{-1}; nmr (CCl_4) τ 5.9 (m, 1 H), 6.6 (s, 1 H), 7.5–9.1 (m, 13 H), 10.1 (m, 1 H).

Anal. Calcd for $C_9H_{16}O$: C, 77.08; H, 11.50. Found: C, 77.11; H, 11.65.

The third product was assigned the structure of 4-(1-ethoxyethyl)bicyclo[6.1.0]nonan-4-ol (**9**): ir (CCl_4) 3570, 3080, 1110 cm^{-1}; nmr (CCl_4) τ 6.1–7.0 (m, 3 H), 7.6–9.0 (broad, 17 H), 9.2 (m, 3 H), 10.15 (m, 1 H); mass spectrum (70 eV) *m/e* 212, 139, 73.

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.70; H, 11.20.

Oxymercuration of Bicyclo[6.1.0]non-4-ene.—To a solution of 3.19 g (0.01 mol) of $Hg(OAc)_2$ in 10 ml of tetrahydrofuran and 10 ml of water was added 1.08 g (0.01 mol) of bicyclo[6.1.0]non-4-ene.[20] The mixture was stirred for 10 min. To the solution was added a 10-ml solution of 3 *M* NaOH and this was followed by a 10-ml solution of 3 *M* $NaBH_4$ in 3 *M* NaOH solution. The mercury was allowed to settle, and the mixture was saturated with NaCl. The upper layer was separated, dried ($MgSO_4$), and concentrated. Glpc analysis indicated that one major fraction is present which has the same retention time and ir spectrum as those of **8**.

Irradiation of 7 in *tert*-Butyl Alcohol.—A sample of 1.24 g of bicyclo[6.1.0]nonan-4-one (**7**) was irradiated through a Corex filter for 3 hr. The solution was then concentrated. Glpc analysis of the crude product on silicone grease (130°) indicated the presence of three products in a ratio of 22:15:62. The first product is believed to be a mixture of the aldehyde **10** and **11**: ir (CS_2) 3080, 3000, 2720, 1730 cm^{-1}; nmr (CCl_4) τ 0.34 (m, 1 H), 3.7–4.7 (m, 1 H) 4.75–5.25 (m, 2 H), 7.2–9.5 (m, 9), 10.05 (m, 1 H). The second product had the same retention time and ir spectrum as **7**.

The third product is believed to be a mixture of the *tert*-butyl esters **12** and **13**: ir (CCl_4) 3070, 2990, 1735, 1400, 1375, 1160 cm^{-1}; nmr (CCl_4) τ 7.6–8.0 (m, 2 H), 8.2–8.9 (15 H), 8.9–9.2 (m, 3 H), 9.35 (m, 3 H), 10.2 (m, 1 H).

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.37; H, 11.05.

Registry No.—**1,** 28399-86-2; **2,** 94-66-6; **3,** 28399-94-2; **4,** 28405-45-0; **6,** 28405-46-1; **7,** 28405-47-2; **8,** 28405-40-5; **9,** 28405-48-3; **14,** 502-49-8; **15,** 28405-49-4; **16,** 5457-66-9; **18,** 28405-50-7; **22,** 28405-52-9.

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[20] H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966).

Notes

Ynamines from 1,1-Difluoro-2-aryl- and -2-alkylethylenes

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The ynamines (**3** and **4**) are a well-known class of organic compounds and have been the subject of a review article.[1] We observed recently that the action of lithium diethylamide on a 1,1-difluoroalkene (**1**) or a β,β-difluorostyrene (**2**) is a convenient, general laboratory route to ynamines (**3** and **4**).[2] **1** and **2** are obtained readily from aliphatic or aromatic aldehydes and sodium chlorodifluoroacetate by the procedure of Fuqua, *et al.*,[3] and an overall yield of 30–40% of the ynamine was obtained from the commercially available aldehyde. The aromatic ynamines were pale yellow liquids, whereas the aliphatic compounds were colorless. All were stable at room temperature and, as expected, each had a characteristic strong band at 2220 cm^{-1} in the infrared spectrum.[1]

$$\underset{\mathbf{1}}{RCH{=}CF_2} + 2LiN(C_2H_5)_2 \longrightarrow \underset{\mathbf{3}}{RC{\equiv}CN(C_2H_5)_2}$$

$$\underset{\mathbf{2}}{ArCH{=}CF_2} + 2LiN(C_2H_5)_2 \longrightarrow \underset{\mathbf{4}}{ArC{\equiv}CN(C_2H_5)_2}$$

The proton and fluorine nmr spectra of **1** and **2** were recorded (Table I). All the spectra were 12-line ABX patterns and were readily interpreted on this basis assuming that $J_{HF}(trans) > J_{HF}(cis)$. It is interesting to note that the chemical shifts of the fluorine atoms of β,β-difluorostyrene are at lower field than those of the 1,1-difluoroalkenes, and, significantly, F-1 (cis to the phenyl ring) is at lower field than F-2 (trans to the phenyl ring). A similar pattern is seen in the pmr spectra of the protonated series where the proton cis to the phenyl ring of styrene appears at lower field than the trans

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[1] H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **6**, 767 (1967).

[2] When this work was initiated, the author was unaware of H. G. Viehe, U. S. Patent 3,369,047 (1968), which claims but does not give examples of the preparation of ynamines from lithium dialkylamides and 1,1-difluoroethylenes.

[3] S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, *J. Org. Chem.*, **30**, 1027 (1965).