Acknowledgments.—The author thanks the National Science Foundation and the Institute of Scientific Research, New Mexico Highlands University, for their support in 1963–1964. She wishes to thank Professor Ernest Wenkert for some of the nmr spectra. This research was also partially supported by grants from the Research Corporation, University of Connecticut Research Foundation, and the Petroleum Research Fund. Grateful acknowledgment is made to the donors of these funds.

Strained Organic Molecules. II. Rearrangements of 1-(1,2,3-Triphenylcycloprop-2-enyl)-3-diazopropan-2-one and (1,2,3-Triphenylcycloprop-2-enyl)acetyl Azide[1,2]

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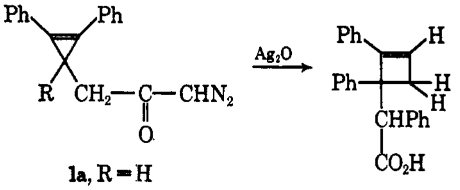
Received August 11, 1967

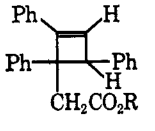
Several reactions are discussed. In the presence of silver benzoate, triethylamine, and ethanol, 1-(1,2,3-triphenylcycloprop-2-enyl)-3-diazopropan-2-one (**1b**) rearranges to two isomers of ethyl (1,2-diphenylcyclobut-2-enyl)phenylacetate (**6a** and **b**). Thermally, (1,2,3-triphenylcycloprop-2-enyl)acetyl azide (**8b**) rearranges to the corresponding isocyanate which was trapped with either dimethylamine or ethanol. With ultraviolet light the azide follows a different pathway.

In the course of our studies on the title rearrangements Masamune and coworkers published several communications[3] on a similar topic. This paper will substantiate and add to the conclusions drawn by his group. The elegant work of Masamune has shown that the product of rearrangement of 1-(1,2,3-triphenylcycloprop-2-enyl)-3-diazopropan-2-one (**1b**) in the presence of silver oxide is to (1,2-diphenylcyclobut-2-enyl)phenylacetic acid (**2**) and not to the tentatively assigned structure, (1,2,4-triphenylcyclobut-2-enyl)acetic acid[1] (**3a**). He also demonstrated that for 1-(2,3-diphenylcycloprop-2-enyl)-3-diazopropan-2-one (**1a**) intermediates in the reaction were 1,2-diphenyltricyclo[2.2.0.0^{2,6}]hexan-3-one (**4a**)[4] and/or phenyl (2-phenylcyclobut-2-enyl)ketene (**5a**).[5]

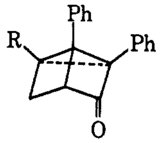


1a, R = H
b, R = Ph

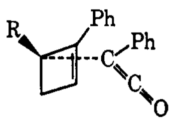
2



3a, R = H
b, R = CH$_2$CH$_3$



4a, R = H
b, R = Ph



5a, R = H
b, R = Ph

In addition to the silver oxide conditions for the Wolff rearrangement of **1b**, silver benzoate, triethylamine, and absolute ethanol have also been utilized.[6] Under the latter conditions the rearrangement also takes place and a 48% yield of crude ester **6a** is isolated. The ester was characterized by spectra, which were similar to the corresponding acid, and analysis. In strong base this ester is converted into a new isomeric compound, **6b**. An nmr spectrum of the crude reaction product from the Wolff rearrangement indicates that **6a** and **b** are present in the ratio of roughly 2:1. Under the reaction conditions both **6a** (containing some **6b**) and **6b** remain essentially unchanged so that **6b** must arise from an intermediate and not from **6a**.

The infrared and ultraviolet spectra of **6a** and **b** are very similar. However, the fact that they are different compounds is evidenced in particular by the nmr spectra. First, the chemical-shift values for the various groups are decidedly different for the two compounds. In fact, a weak absorption for the ethyl group in **6b** can be seen clearly in the spectrum of impure **6a**. Moreover, the absorption for the ethyl group in the two compounds is decidedly different. For compound **6a** this absorption is a simple A_2X_3 pattern, whereas for compound **6b** the pattern is that for an ABX_3 system (see Experimental Section). Thus the differing asymmetry of the two molecules affects the nmr pattern for the ethyl group. The conclusion drawn from the spectral and chemical data is that the two compounds must be racemic diastereomers differing in the configuration of the carbon α to the carbonyl group.

The preferential formation of **6a** can be explained by a stereoselective reaction of either 1,2,6-triphenyltricyclo[2.2.0.0^{2,6})hexan-3-one (**4b**) (postulated in analogy

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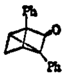
(1) A preliminary communication of part of this work appeared in A. Small, *J. Amer. Chem. Soc.*, **86**, 2091 (1964).

(2) Abstracted in part from the Master's thesis of S. Tang, University of Connecticut, June 1966.

(3) (a) S. Masamune and N. C. Castellucci, *Proc. Chem. Soc.*, 298 (1964); (b) S. Masamune and K. Fukumoto, *Tetrahedron Lett.*, 4647 (1965); (c) N. C. Castellucci, M. Kato, H. Zenda, and S. Masamune, *Chem. Commun.*, 473 (1967).

(4) A referee has suggested 2,4-diphenyltricyclo[2.2.0.0.^{2,5}]hexan-3-one (i) as an alternative structure to **4a**. With the information available, the authors cannot unequivocably decide between i and **4a**; the nmr data[3b] and



i

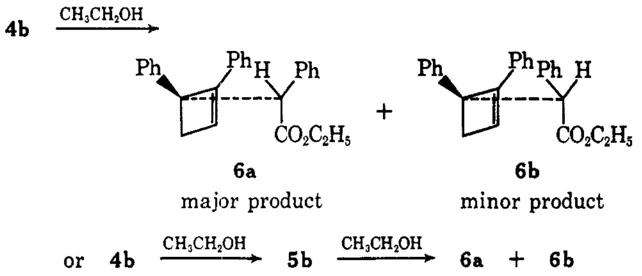
the results of the application of Occam's Razor to the mechanism of formation seem more compatible with **4a**.

(5) For convenience only one member of each *dl* pair is drawn.

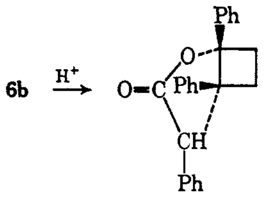
(6) M. S. Newman and P. F. Beal, *J. Amer. Chem. Soc.*, **72**, 5163 (1950).

to Masamune's findings[3b]) or the corresponding ketene **5b** with ethanol. These reactions are depicted in Scheme I.[5]

SCHEME I



In addition to the evidence which Masamune has presented for the structure of compound **2** and related compounds[3b] is the rearrangement of **6b** in acid to compound **7** in 91% yield.

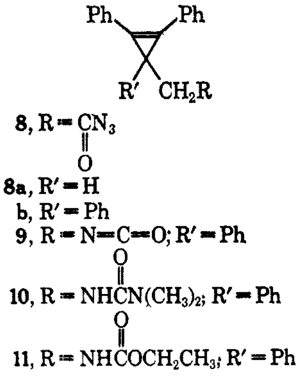


7

Assignment of the structure of **7** rests on its spectra and analysis. The infrared spectrum indicates a γ-lactone (carbonyl band at 1780 cm^{-1}) while the ultraviolet spectrum shows the loss of the phenyl-conjugated double bond (only end absorption). The nmr spectrum substantiates structure **7**. In particular, besides the phenyl absorption, the lowest field absorption was expected to be that for protons on the carbon α to the carbonyl group. This absorption, occurring at 4.4 ppm, is a *one-proton singlet* rather than the complex spectrum expected for the lactone derived from **3b**.

Because of the enlightening chemistry of **1b**, the reactions of (1,2,3-triphenylcycloprop-2-enyl)acetyl azide (**8b**) were studied. During the course of our investigation, Masamune and coworkers reported[3b,c] on the thermal and photoreactions of (2,3-diphenylcycloprop-2-enyl)acetyl azide (**8a**). Our work provides a series of compounds which undergo analogous reactions but unfortunately do not shed any additional light on their mechanisms.

The azide **8b** was prepared from (1,2,3-triphenylcycloprop-2-enyl)acetyl chloride and sodium azide.[7] The azide rearranged thermally in refluxing benzene to the corresponding isocyanate **9**, which could be trapped with dimethylamine to give N,N-dimethyl-N′-(1,2,3-triphenylcycloprop-2-enylcarbinyl)urea (**10**) and with ethanol to give two products, ethyl N-(1,2,3-triphenylcycloprop-2-enylcarbinyl)carbamate (**11**) and 3,4,5-triphenyl-2-pyridone (**12**).[9] The structures of **10** and **11** were straightforwardly assigned on the basis of the typical diphenylcyclopropene chromophore in the ultraviolet spectrum, nmr and infrared spectra, and analysis. The structure of **12** was assigned on the basis of the infrared peaks at 3450 (N—H) and 1630 cm^{-1} (C=O), ultraviolet absorption at λ_{max} 326 mμ (log ε 3.92) and 255 (4.33), and analysis. The spectra are qualitatively similar to those reported for 3,4-diphenyl-2-pyridone[3b] and 5,6-diphenyl-2-pyridone[10] and to those for 4,5,6-triphenyl-2-pyridone (see below). The mechanism of pyridone formation in a similar case has been discussed by Masamune.[3c]



$\mathbf{8}, R = \underset{\underset{O}{\|}}{C}N_3$

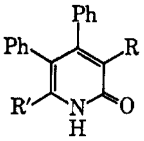
$\mathbf{8a}, R' = H$

$\mathbf{b}, R' = Ph$

$\mathbf{9}, R = N{=}C{=}O; R' = Ph$

$\mathbf{10}, R = NH\overset{\overset{O}{\|}}{C}N(CH_3)_2; R' = Ph$

$\mathbf{11}, R = NH\overset{\overset{O}{\|}}{C}OCH_2CH_3; R' = Ph$



12, R = Ph, R′ = H
13, R = H, R′ = Ph

Photolysis of **8b** in anhydrous ether gave considerably different results. Besides intractable tars, there was obtained 4,5,6-triphenyl-2-pyridone (**13**). Some **9** was also present (presumably from thermal rearrangement of the azide) which could be trapped with ethanol to give a very low yield of **11**. Irradiation of **9** did not give any **13**. The structure of **13** was indicated by its spectra and analysis (see Experimental Section) and its identity with a sample prepared by a different route.[11] No intermediate was detected in this reaction by removing aliquots and taking nmr and infrared spectra. Masamune[3c] has discussed the mechanism of this reaction with **8a** as starting material.

Experimental Section

The nmr spectra were run on a Varian A-60 spectrometer in deuteriochloroform with tetramethylsilane as an internal standard. Ultraviolet spectra were determined either on a Beckman DK or Cary 14 spectrophotometer with 95% ethanol as the solvent unless otherwise indicated. Infrared spectra were taken as potassium bromide disks or smears on either a Beckman IR-9 or Perkin-Elmer Infracord. Melting points are uncorrected.

Rearrangement of 1-(1,2,3-Triphenylcyclopropenyl)-3-diazopropan-2-one (1b) to (1,2-Diphenylcyclobut-2-enyl)phenylacetic Acid (2) in Dioxane-Water.—The diazo ketone **1b**, prepared from 1.5 g (0.0046 mol) of (1,2,3-triphenylcycloprop-2-enyl)-acetic acid,[8] was dissolved in 35 ml of purified dioxane and added dropwise with stirring to 0.300 g (0.0013 mole) of silver oxide, 0.510 g (0.0048 mol) of sodium carbonate, and 0.300 g (0.0019 mol) of sodium thiosulfate dissolved in 30 ml of water main-

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(7) The chloride was prepared in the usual manner,[8] the azide by the method of W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Amer. Chem. Soc.*, **85**, 2754 (1963).

(8) See paper I in this series, A. S. Monahan, *J. Org. Chem.*, **33**, 1441 (1968).

(9) A referee has suggested 3,5,6- or 3,4,6-triphenyl-2-pyridone as alternative structures. Although the 3,4,5 arrangement of phenyls is not established by our data, it is the most likely on mechanistic grounds and in view of Masamune's work with **8a**.[3b,d]

(10) A. D. Campbell and K. D. R. Stevens, *J. Chem. Soc.*, 949 (1956).

(11) The synthesis was patterned after the pyridone synthesis of C. Hauser and C. J. Eby, *J. Amer. Chem. Soc.*, **79**, 728 (1957).

tained at 50–60° with an oil bath.[12] The addition took 0.5 hr, and the reaction mixture was heated an additional 0.5 hr. The reacion mixture was filtered and the filtrate extracted three times with ether. The basic filtrate was then acidified with dilute nitric acid and extracted three times with ether. The ether was washed with water, dried over magnesium sulfate, filtered, and removed under reduced pressure to give 0.487 g of oil. Treatment with ethanol gave 0.174 g (11%) of colorless crystals of **2**, mp 175–179, and a second crop of 0.219 g (14%), mp 152–168°.

The ether extracts of the original filtrate were combined, washed with water, dried over sodium sulfate, filtered, and removed under reduced pressure to give 1.09 g of dark oil. This nonacidic material was run through the reaction again using the same quantities of dioxane–water and inorganic reagents and heating at 70–80° for 5.5 hr. Work-up as above gave 0.202 g (13%) of **2**, mp 165–171°.

A sample of **2**, recrystallized for analysis from ethanol, had mp 178.5–180°; ultraviolet, λ_{max} 257 mμ (log ε 4.12); infrared, 1710 cm^{-1} (C=O); nmr, δ 10.1 (s, 1, acid hydrogen), 7.2 (m, 15, phenyl hydrogens), 6.2 (somewhat broad s, 1, vinyl hydrogen), 4.6 (somewhat broad s, 1, tertiary hydrogen), 3.4 (d, 1, J = 14 cps, methylene hydrogen), 2.6 (d, 1, J = 14 cps, methylene hydrogen).

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.42; H, 5.78.

Rearrangment of 1b to 6a and 6b in Ethanol.—To 1.5 g (0.0043 mol) of **1b** suspended in 60 ml of absolute ethanol was added several drops at a time over a period of 1.5 hr, 0.6 g of silver benzoate dissolved in 6 ml of triethylamine. Most gas evolution ceased after the first 0.5 hr. The reaction mixture was stirred an additional 1.5 hr, poured into water, extracted three times with ether, washed three times with hydrochloric acid, then three times with water, dried over magnesium sulfate, filtered, and removed under reduced pressure to give a red oil. The oil was chromatographed on silica gel to give 0.756 g (48%) of colorless crystalline **6a**, mp 100–106°.

A sample, recrystallized for analysis from ethanol, had mp 98.5–126°; ultraviolet, λ_{max} 256 mμ (log ε 4.13); infrared, 1730 cm^{-1} (C=O); nmr (in addition there were very weak peaks of **6b**), δ 7.3 (m, 16, phenyl hydrogens), 6.5 (t, 1, J = 1 cps, vinyl hydrogen), 4.7 (s, 1, tertiary hydrogen), 3.9 (q, 2, J = 7 cps, methylene of ethyl), 2.7 (q, 1, J = 1 cps, J = 13 cps, ring methylene hydrogen), 0.9 (t, 3, J = 7 cps, methyl hydrogens), 3.5 (d, 0.5, J = 1 cps, upperfield part of quartet due to other ring methylene hydrogen). The lower field portion of the latter absoption is hidden by the quartet at 3.9 ppm.)

Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 84.90; H, 6.50.

To 0.075 g of **6a** was added 25 ml of ethanol containing 6 g of dissolved potassium hydroxide. The mixture was allowed to stand 1 day at room temperature, then poured into water. The water layer was extracted three times with ether which was washed with water, dried over magnesium sulfate, filtered, and removed under reduced pressure. The resulting solid was recrystallized from ethanol to give 0.045 g, mp 130–132°, and a second crop of 0.022 g, mp 95–99°. The first crop, **6b**, recrystallized for analysis from ethanol, had mp 132.5–136°. Admixture with **6a** gave mp 94–124°. The ultraviolet had λ_{max} 259 mμ (log ε 4.18); infrared identical with that of **6a** except that peak at 1200 cm^{-1} was stronger; nmr, δ 7.4 (m, 15, phenyl hydrogens), 6.2 (t, 1, J = 1 cps, vinyl hydrogen), 4.2 (q of d, 2, J = 7 cps, J = 3 cps, methylene of ethyl group), 3.4 (d of d, 1, J = 16 cps, J = 1 cps, ring methylene hydrogen) and 1.1 (t, 3, J = 7 cps, methyl of ethyl group).

Anal. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.57. Found: C, 84.84, 84.60; H, 6.59, 6.63.

The nmr spectrum of the crude reaction product from another run of the rearrangement of **1b** (acidic material was removed from the ether solution by extraction wih 10% sodium carbonate) was taken. The ratio of the peaks for the methine protons was roughly 2:1 **6a**/**6b**.

Attempted Equilibration of 6a and 6b under Wolff Rearrangement Conditions.—To a flask was added 0.103 g of **6b**, 0.040 g of silver benzoate, 4 ml of ethanol, and 0.4 ml of triethylamine. Since heat was necessary to keep **6b** in solution, the mixture was refluxed for 0.5 hr and then allowed to stand at room temperature for 2.5 hr during which time a solid precipitated. The reaction mixture was worked up in the same way as the run with compound **1b** except that any acidic material was removed by extraction of the ether solution with two portions of 10% sodium carbonate. The nmr spectrum of the crude product was identical with that of the starting material. No peaks for compound **6a** could be detected.

A 0.102-g sample of **6a**, which by integration of the vinyl and methine hydrogens in the nmr spectrum indicated a ratio of **6a**/**6b** of 2.2 (±0.2):1, was mixed with 0.040 g of silver benzoate, 4 ml of ethanol, and 0.4 ml of triethylamine. The mixture was warmed to get the solid into solution, then allowed to stand at room temperature for 3.5 hr. After a work-up as for **6b**, the nmr spectrum showed a ratio of **6a**/**6b** of 2.1 (±0.2):1.

Rearrangement of 6b to Lactone 7.—To 1.011 g (0.00274 mol) of compound **6b**, mp 135–136°, was added 100 ml of acetic acid, 30 drops of water, and 11 drops of sulfuric acid. The mixture was refluxed for 6 hr and poured onto ice. The resulting mixture was extracted three times with ether, which was washed with water, 10% sodium carbonate, and water, dried over magnesium sulfate, filtered, and removed under reduced pressure to give an oily solid. This was recrystallized once from ethanol to give 0.71 g of **7**, mp 129–131°, and 0.126 g, mp 126–131°, or a total of 0.845 g (91%).

A sample, recrystallized for analysis from ethanol, had mp 135–137°; ultraviolet, only end absorption; infrared, 1780 cm^{-1} (C=O); nmr, δ 7.0 (m, 15, phenyl hydrogens), 4.4 (s, 1, tertiary hydrogen), 2.6 (m, 4, methylene hydrogens).

Anal. Calcd for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.40, 84.49; H, 5.70, 5.86.

(1,2,3-Triphenylcycloprop-2-enyl)acetyl Azide (8b).—The acid chloride[1] from 0.40 g (0.0012 mol) of (1,2,3-triphenylcycloprop-2-enyl)acetic acid, prepared in the usual manner,[8] was dissolved in 8 ml of dry acetone and cooled in an ice bath. To the cold solution was rapidly added 0.080 g (0.0012 mol) of sodium azide dissolved in a minimum amount (about 0.5 ml) of water. The solution was stirred for 1 hr and poured into ice-cold water. The resulting mixture was extracted with ether which was washed once with water, dried over magnesium sulfate at 0°, filtered, and removed under reduced pressure to give **8b**: infrared, 2130 (N=N), 1710 (C=O), and 1800 cm^{-1} (cyclopropene); nmr, δ 7.2 (m, 15, phenyl hydrogens), 3.2 (s, 2, methylene hydrogens). The compound rearranged slowly at room temperature to the corresponding isocyanate **9**.

N,N-Dimethyl-N′-(1,2,3-triphenylcycloprop-2-enylcarbinyl)-urea (10).—An ether solution of **8b** [from 0.3 g of (1,2,3-triphenylcycloprop-2-enyl)acetic acid] was added dropwise to 4 ml of stirred refluxing benzene over the course of 30 min. The solution was refluxed for 20 min more and cooled in an ice bath, and anhydrous dimethylamine passed through for 1 hr. Ether was added to the solution which was washed with water to remove excess dimethylamine, then dried over magnesium sulfate, filtered, and removed under reduced pressure to give 0.294 g of yellow oil. Crystallization from ethyl acetate gave a first crop of 0.044 g of colorless **8b**, mp 118–119°, and a second crop of 0.122 g of yellow crystals, mp 116–120°. The total yield was 0.116 g (49%).

A sample prepared for analysis had mp 120–120.5°; ultraviolet, λ_{max} 330 mμ (log ε 4.32), 315 (4.41), sh 299 (4.34); infrared, 3400 (N-H), 1800 (cyclopropene), 1620 cm^{-1} (C=O); nmr, δ 7.4 (m, 16, phenyl hydrogens and N-H), 4.3 (broad s, 2, methylene hydrogens), 2.6 (s, 6, methyl hydrogens).

Anal. Calcd for $C_{25}H_{24}N_2O$: C, 81.52; H, 6.52; N, 7.60. Found: C, 81.63; H, 6.73; N, 7.85.

Ethyl N-(1,2,3-Triphenylcycloprop-2-enylcarbinyl)carbamate (11) and 3,4,5-Triphenyl-2-pyridone (12).—A dry ether solution of **8b** (from 0.41 g of acid chloride) was added dropwise to 8 ml of refluxing, stirred, dry benzene over the course of 20 min. After the addition was complete, the benzene–ether solution was refluxed for an additional 25 min. The solvent was evaporated and a yellow oil obtained: ultraviolet, λ_{max} 330 mμ (log ε 4.27), 317, 299; infrared, 2275 cm^{-1} (isocyanate). Absolute ethanol (25 ml) was added to the oil and the resulting solution allowed to stand at room temperature for 15 hr. The solvent was removed under reduced pressure to give 0.43 g of brown solid. By fractional crystallization from benzene and ethanol, there was obtained 0.29 g (64%) of **11**, mp 114–116°, and 0.029 g (8%) of **12**, mp 317–320. Another run gave 70% **11**, mp 115–116°, and 6% **12**.

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[12] See W. E. Bachmann and W. S. Strove, *Org. Reactions*, **1**, 51 (1942).

A sample of **11**, prepared for analysis by recrystallization from ethanol, had mp 117.5–118°; ultraviolet, λ_{max} 330 mμ (log ϵ 4.33), 314 (4.43), sh 299 (4.36); infrared, 3300 (N–H), 1800 (cyclopropene), 1690 cm^{-1} (C=O); nmr, δ 7.4 (m, 16, phenyl hydrogens and N–H), 4.3 (d, 2, J = 5 cps, methylene attached to ring), 4.0 (q, 2, J = 7 cps, methylene of ethyl), 1.1 (t, 3, J = 7 cps, methyl of ethyl).

Anal. Calcd for $C_{25}H_{23}NO_2$: C, 81.30; H, 6.28; N, 3.79. Found: C, 81.12; H, 6.32; N, 3.75.

A sample of **12** prepared for analysis by recrystallization from acetone had mp 323.5–325°; ultraviolet, λ_{max} 326 mμ (log ϵ 3.92), 255 (4.33); infrared, 2450 (N–H), 1630 cm^{-1} (C=O).

Anal. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30. Found: C, 85.39; H, 5.38.

Photolysis of Azide 8b.—An anhydrous ether solution (200 ml) of **8b** (from 0.35 g of acid chloride) was irradiated in a quartz cell under positive nitrogen pressure. A Srinivasan–Griffin reactor with 2537-Å lamps was used as a light source. The disappearance of the azide bands in the infrared spectrum was complete after 6 hr. After allowing some solvent to evaporate, there was obtained 0.025 g of colorless fluffy crystals, mp 272–275°; a second crop gave 0.013 g, mp 268–271°; a third crop gave 0.008 g, mp 267–271°. The total yield of 4,5,6-triphenyl-2-pyridone (**13**) was 0.046 g (14%). A mixture melting point with **13**, mp 276–277°, prepared by a different route (see below), was 275–276°. The infrared spectra of the two samples were also identical.

A sample prepared for analysis by recrystallization from acetone had mp 276–277°; ultraviolet, λ_{max} 326 mμ (log ϵ 3.91), 259 (4.25); infrared, 2450 (N–H), 1635 cm^{-1} (C=O).

Anal. Calcd for $C_{23}H_{17}NO$: C, 85.42; H, 5.30; N, 4.33. Found: C, 85.31; H, 5.30; N, 4.14.

The remainder of the reaction mixture was evaporated to a yellow oil, whose infrared showed a band at 2270 cm^{-1} (isocyanate). Absolute ethanol was added to the oil and after 4 days was removed under reduced pressure. The resulting gum was chromatographed on Fisher adsorption alumina giving 0.005 g (2%) of **11**, mp 115–117°. The rest of the material was an intractable red gum.

Photolysis of 1,2,3-Triphenylcycloprop-3-enylcarbinyl Isocyanate (9).—An anhydrous ether solution of **8b** (from 0.385 g of acid chloride) was added dropwise to 20 ml of refluxing dry benzene over the course of 5 min. It was then refluxed an additional 1 hr. The solvents were evaporated under reduced pressure to give a brown oil whose infrared spectrum showed a band at 2270 cm^{-1}. The oil was dissolved in 200 ml of anhydrous ether and photolyzed for 6 hr. The solvent was evaporated leaving an oil which showed a peak at 2270 cm^{-1} (isocyanate). Absolute ethanol was added to the oil and the solution allowed to stand at room temperature for 4 days. By filtering, 0.032 g (9%) of **12**, mp 315–318°, was obtained. Chromatography of the remaining material on Fisher adsorption alumina gave 5% (0.020 g) of **11**, mp 116–118°. The rest of the material was an intractable red gum.

No pyridone could be obtained before treating the reaction mixture with ethanol.

Preparation of 4,5,6-Triphenyl-2-pyridone (13).[11]—To 75 g of stirred polyphosphoric acid was added 3.6 g (0.025 mol) of 3-phenyl-3-oxopropanenitrile and 5.0 g (0.025 mol) of deoxybenzoin. The mixture was stirred for 5 min and then heated and stirred on a steam bath for 30 min during which time the reaction mixture turned red. Another 5 g of deoxybenzoin was added and the mixture heated at 135–145° in an oil bath for 35 min. The mixture was poured onto 300 g of ice. To this was added 200 ml of ether, and the mixture was stirred for 0.5 hr. The mixture was filtered to give a solid which on recrystallization from acetone gave 0.037 g (0.48%) of **13**, mp 276–277°.

Registry No.—**1b**, 15707-48-9; **2**, 15983-99-0; **6a**, 15983-93-4; **6b**, 15983-94-5; **7**, 15983-95-6; **8b**, 15983-96-7; **10**, 15983-97-8; **11**, 15983-98-9; **12**, 15984-00-6; **13**, 15984-01-7.

Acknowledgments.—The authors wish to thank the National Science Foundation and the Institute of Scientific Research, New Mexico Highlands University, for their support in 1963–1964. We wish to thank Professor Ernest Wenkert for some of the nmr spectra. This research was also partially supported by grants from the Research Corporation, University of Connecticut Research Foundation, and the Petroleum Research Fund. Grateful acknowledgment is made to the donors of these funds.

Reactive Intermediates in the Bicyclo[3.1.0]hexyl and Bicyclo[3.1.0]hexylidene Systems. IV.[1] The Free-Radical Chlorination and Chloroformylation of Bicyclo[3.1.0]hexane

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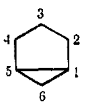
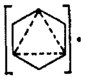
Received September 25, 1967

Free-radical chlorination of bicyclo[3.1.0]hexane (I) using *t*-butyl hypochlorite results in substitution at C-2 (78%) and C-3 (22%). Radical chloroformlyation of I using oxalyl chloride generates, after esterification, 2-carbomethoxy- (16%) and 3-carbomethoxybicyclo[3.1.0]hexane (12%) derivatives, as well as rearrangement products methyl Δ^2-cyclopentenylacetate (36%) and 4-carbomethoxycyclohexene (33%).

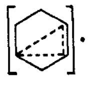
Our interest in bicyclo[3.1.0]hexyl carbonium ions[1,3] and bicyclo[3.1.0]hexylidene bivalent carbon intermediates[4] led us quite naturally to a consideration of bicyclo[3.1.0]hexyl free-radical intermediates. Hydrogen abstraction from bicyclo[3.1.0]hexane (I) appeared to be a straightforward method of generation of bicyclo[3.1.0]hexyl free radicals. Abstraction of a hydrogen atom from C-3 might produce free radical II, analogous to the trishomocyclopropenyl carbonium ion,[5] while abstraction at C-2 might generate radical III, analogous to a bicyclobutonium ion intermediate.[6] We chose to consider free-radical halogenation using



I



II



III

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