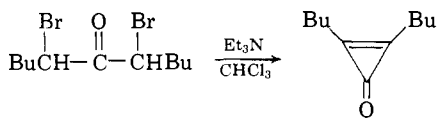


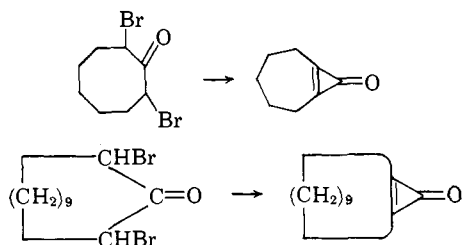


details of this speculative step are best left unspecified, it could involve simple displacement, vinylcyclopropanone formation, or production of a zwitterion related to that which is involved in some Favorskii reactions.<sup>7</sup> When the cyclopropanone synthesis was conducted in  $\text{CHCl}_3$  containing ethanol, some ethyl 2-propylhex-2-enoate was also formed.

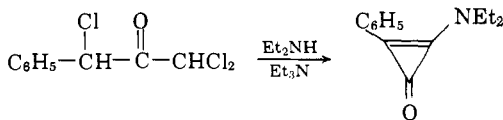
Di-*n*-butylcyclopropanone was prepared by a similar dehydrobromination of di(bromo-*n*-amyl) ketone.



Application of the reaction to di(bromoethyl) ketone apparently led to dimethylcyclopropanone, with expected infrared bands at 1850 and 1650  $\text{cm}^{-1}$  and a sharp n.m.r. singlet at  $\tau$  7.75, but in spite of repeated attempts this material could not be obtained analytically pure. Dibromocyclooctanone was converted to cycloheptenocyclopropanone in high (56%) yield; cycloundecenocyclopropanone was prepared similarly.



An attempt to prepare phenylhydroxycyclopropanone<sup>8</sup> (via intermediate phenylchlorocyclopropanone) by dehydrochlorination of a mixture of trichlorophenylacetones failed, no strong absorption near 1850  $\text{cm}^{-1}$  being evident, but when the dehydrochlorination was run in the presence of diethylamine, some phenyldiethylaminocyclopropanone was isolated. The struc-



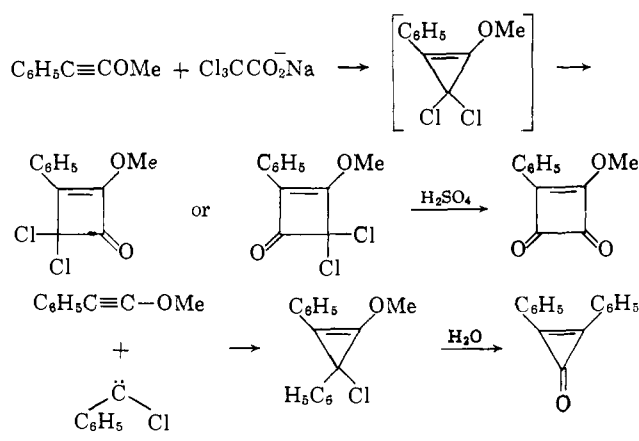
ture was established by analysis, a typical cyclopropanone infrared spectrum with bands at 1850 and 1630  $\text{cm}^{-1}$ , and the n.m.r. spectrum; the latter showed nonequivalent ethyl groups, indicating strong conjugation by the amino group. The latter was also indicated by the striking resistance of the compound to all attempted hydrolyses to phenylhydroxycyclopropanone.

An alternative approach to this system involved carbene additions to phenylmethoxyacetylene. Thus "phenylchlorocarbene" added readily to afford diphenylcyclopropanone. Reaction of the acetylene with sodium trichloroacetate, however, afforded as the only isolable product a phenylmethoxydichlorocyclobutenone; the latter was converted to known<sup>9</sup> phenylmethoxycyclobutenedione.

(7) Cf. A. Fort, *J. Am. Chem. Soc.*, **84**, 2620 (1962).

(8) D. Farnum and P. Thurston, *ibid.*, **86**, 4206 (1964), describe a compound to which they assign this structure.

(9) E. Smutny, M. Caserio, and J. D. Roberts, *ibid.*, **82**, 1793 (1960).



2. *Properties.* All of the cyclopropanones have infrared absorptions near 1850 and 1620  $\text{cm}^{-1}$  which have been tentatively ascribed<sup>10</sup> to the  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  stretches, respectively. In the ultraviolet the dialkylcyclopropanones show only strong end absorption for the  $\pi \rightarrow \pi^*$  transition whose maximum lies below 175  $\text{m}\mu$ ; the  $n \rightarrow \pi^*$  transition could not be detected with high concentrations in a variety of solvents, although it was later<sup>10</sup> found near 250  $\text{m}\mu$  ( $\text{CH}_2\text{Cl}_2$ ). Both of these results are consistent with the predictions of simple molecular orbital theory: a large amount of energy is needed to promote an electron from the stable bonding orbital of this aromatic system to an unstable antibonding orbital in a  $\pi \rightarrow \pi^*$  transition, and even the  $n \rightarrow \pi^*$  transition should be at rather low wave length ( $\sim 250$   $\text{m}\mu$ ) because of the relatively high energy of the cyclopropanone antibonding orbital.

The dipole moment<sup>11</sup> of dipropylcyclopropanone is 4.78 D. and of cycloheptenocyclopropanone, 4.66 D. These are smaller than the 5.14 D. of diphenylcyclopropanone<sup>11</sup> (lit.<sup>12</sup> 5.08 D.) but this probably does not mean a less polar structure for the alkylcyclopropanones. The dipole moment of the diphenyl compound will be larger even with a smaller contribution of charge-separated resonance forms, since delocalization into the phenyl rings increases the length of the dipole.

The basicity of dipropylcyclopropanone was determined by examining the n.m.r. chemical shift in the propyl group as a function of  $H_0$  of the solvent, aqueous  $\text{H}_2\text{SO}_4$ . Although the ketone did not behave as a Hammett base, a rough titration curve was obtained with a midpoint (half protonation) at  $H_0 = -1.9 \pm 0.3$ . This can be compared with a "pK" of  $-2.5 \pm 0.3$  for diphenylcyclopropanone, indicating that the dialkyl ketone is a bit more basic.

The n.m.r. spectrum of dipropylcyclopropanone shows that it does not strongly resemble a cyclopropanone. Thus the two  $\text{CH}_2$  units in propyl groups of dipropylcyclopropenyl cation, tripropylcyclopropenyl cation, and diphenylpropylcyclopropenyl cation are separated<sup>13</sup> by 1.27–1.30 p.p.m. while in dipropylcyclopropanecarboxylic acid the separation is 0.80 p.p.m. In dipropylcyclopropanone the separation is

(10) A. Krebs, *Angew. Chem. Intern. Ed. Engl.*, **4**, 10 (1965), and private communication.

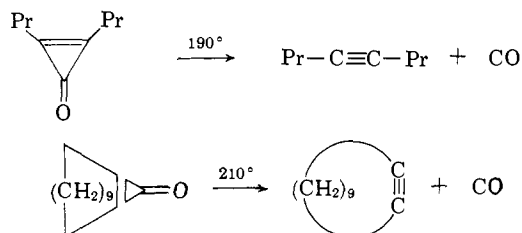
(11) Dipole moments were calculated using the method of E. Guggenheim, *Trans. Faraday Soc.*, **45**, 714 (1949). Details may be found in the thesis of J. Posner, Columbia University, 1964.

(12) Cited in ref. 2b.

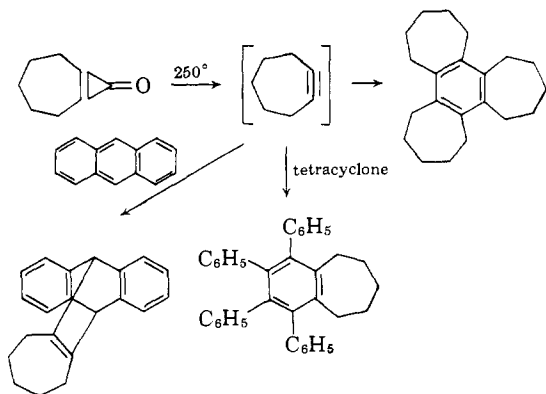
(13) R. Breslow, H. Höver, and H. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962).

0.85 p.p.m., so it closely resembles a covalent cyclopropene as far as charge next to the propyl group is concerned.

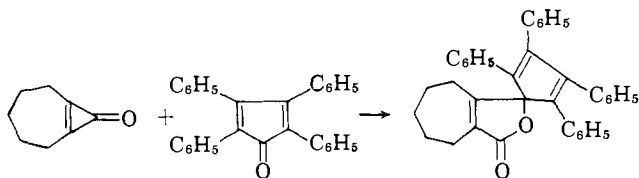
3. *Reactions.* Pyrolysis of dipropylcyclopropenone at 190° afforded dipropylacetylene and CO. The first-order rate constant for this process,  $0.042 \pm 0.010 \text{ min.}^{-1}$ , was 20% of that for diphenylcyclopropenone pyrolysis under the same conditions. Similarly, pyrolysis of cycloundecenocyclopropenone at 210° afforded a 93% yield of cycloundecyne.



Pyrolysis of cycloheptenocyclopropenone at 250° produced CO and a 16% yield of triscycloheptenobenzene. This presumably arises from intermediate cycloheptyne, an unstable acetylene.<sup>14</sup> Pyrolysis of the cyclopropenone in the presence of tetracyclone affords 1,2-cyclohepteno-3,4,5,6-tetraphenylbenzene; an adduct of cycloheptyne to anthracene has been prepared in a similar manner. The pyrolysis with tetracy-



clone also led to a 1:1 adduct, to which we have assigned the structure shown.



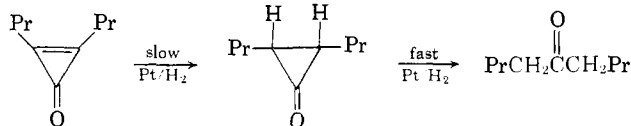
Several careful attempts were made to effect the pyrolysis of cycloheptenocyclopropenone in a gas phase flow system, passing the ketone rapidly through a hot zone and thence into a trap containing phenyl azide or tetracyclone. No evidence could be obtained from these experiments that cycloheptyne survives long enough to be detected and examined in our apparatus. Attempts at flash photolysis<sup>15</sup> of the ketone have also so far proved unsuccessful.

Hydrogenation of dipropylcyclopropenone was examined in order to learn whether in this series as well

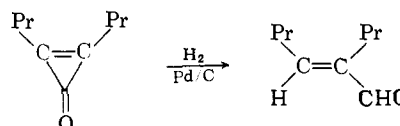
(14) Cf. G. Wittig, *Angew. Chem.*, 74, 479 (1962); F. G. Willey, *ibid.*, 76, 144 (1964).

(15) By Professor R. S. Berry of the University of Chicago.

hydrogenolysis of the cyclopropanone intermediate<sup>1b</sup> would be faster than the first reduction. With platinum in dioxane, after absorption of 1 mole of H<sub>2</sub>, a large amount of cyclopropenone could still be detected spectroscopically and the major product was di-*n*-butyl ketone, from double reduction.

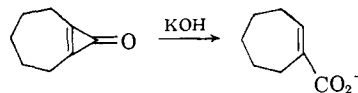


With palladium on carbon, on the other hand, the cyclopropenone was essentially gone after absorption of 1 mole of H<sub>2</sub>, and the major product was 2-propyl-2-hexenal, from hydrogenolysis of the C-CO bond.



Selection between these two paths was not complete; platinum afforded some unsaturated aldehyde (and saturated aldehyde from further reduction), while Pd-C yielded a little di-*n*-butyl ketone (and saturated aldehyde). In no case could a cyclopropanone be detected spectroscopically.

The dialkylcyclopropenones are much more stable to alkaline hydrolysis than is diphenylcyclopropenone.<sup>1b</sup> However, cycloheptenocyclopropenone was cleaved to the expected acid with refluxing 10% KOH.



## Experimental

1. *Syntheses.* A. *Dipropylcyclopropenone from Dipropylacetylene.* A mixture of 38 g. of distilled octyne-4 (0.345 mole) and 80 g. of sodium trichloroacetate (0.432 mole) in 200 ml. of dimethoxyethane was heated at reflux under N<sub>2</sub> until all CO<sub>2</sub> evolution had ceased. Work-up with CH<sub>2</sub>Cl<sub>2</sub> and water afforded 12.21 g. of a mixture, b.p. 65–85° (0.3 mm.), with infrared absorption at 1840 and 1790 cm.<sup>-1</sup> (also present in the reaction mixture before work-up). The mixture was taken up in 50 ml. of CH<sub>2</sub>Cl<sub>2</sub> and extracted with four 10-ml. portions of 65% H<sub>2</sub>SO<sub>4</sub>. The acid layer was neutralized and the product was isolated and distilled to yield 4.23 g. (0.030 mole, 8.9% based on octyne-4) of *dipropylcyclopropenone*, b.p. 80° (0.7 mm.).

*Anal.* Calcd. for C<sub>9</sub>H<sub>14</sub>O: C, 78.21; H, 10.21. Found: C, 77.99, 78.47; H, 10.34, 10.34.

In the infrared (CCl<sub>4</sub>) the compound showed two strong bands at 1840 and 1630 cm.<sup>-1</sup>. The ultraviolet spectrum (ethanol) showed only end absorption,  $\epsilon_{215 \text{ m}\mu}$  540; the  $\lambda_{\text{max}}$  was below 175 m $\mu$ . The n.m.r. spectrum in CCl<sub>4</sub> (vs. Me<sub>4</sub>Si) showed three sets of peaks: a triplet at  $\tau$  8.95 ( $J = 7$  c.p.s.), a sextuplet at 8.27 ( $J = 7$  c.p.s.), and a triplet at 7.42 ( $J = 7$  c.p.s.) with relative areas 3:2:2.

The methylene chloride fraction above yielded 5.44 g. (7% based on octyne-4) of 4,4-dichlorodipropylcyclo-

butenone, b.p. 80° (0.3 mm.). Despite repeated attempts this material could not be completely purified.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>Cl<sub>2</sub>O: C, 54.32; H, 6.38; Cl, 32.06. Found: C, 53.59; H, 5.96; Cl, 33.09.

In the infrared (CCl<sub>4</sub>) the compound showed absorption at 1790 and 1610 cm.<sup>-1</sup>. The n.m.r. spectrum showed two overlapping propyl patterns, with triplets at  $\tau$  7.30 and 7.75 ( $J = 7$  c.p.s.), an apparent septuplet at 8.33 ( $J = 7$  c.p.s.), and a quartet at 9.00 (two overlapping triplets).

When 2.18 g. of the above dichloro ketone was heated for 2 hr. at 100° with 25 ml. of 90% H<sub>2</sub>SO<sub>4</sub> under N<sub>2</sub>, it yielded 0.720 g. (43%) of a yellow liquid, b.p. 70° (0.2 mm.), identified as 1,2-dipropylcyclobutenedione.

*Anal.* Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>2</sub>: C, 72.26; H, 8.48. Found: C, 72.20; H, 8.37.

In the infrared<sup>16</sup> (neat) the compound showed bands at 1784, 1763, and 1589 cm.<sup>-1</sup>. The n.m.r. showed a single propyl group, with a triplet at  $\tau$  7.25, a sextuplet at 8.25, and a triplet at 9.03, all with  $J = 7$  c.p.s. and areas in a ratio of 2:2:3. The ultraviolet spectrum (95% EtOH) showed  $\lambda_{\max}$  218 m $\mu$  ( $\epsilon$  18,000) and a shoulder at 355 m $\mu$  ( $\epsilon$  28).

A 20% yield of 4,4-dichlorodipropylcyclopropenone was obtained when 13 g. of dipropylcyclopropenone was treated with 49 g. of sodium trichloroacetate in 100 ml. of dimethoxyethane as above.

#### B. Dipropylcyclopropenone from Di-n-butyl Ketone.

A solution of 320 g. (2.0 moles) of Br<sub>2</sub> in CHCl<sub>3</sub> was added over 1 hr. to 142 g. (1.0 mole) of di-n-butyl ketone in 1 l. of CHCl<sub>3</sub>. After standing overnight the solution was dried and distilled, yielding 211 g. (71%) of the dibromo ketone mixture, b.p. 132–135° (20 mm.).

*Anal.* Calcd. for C<sub>9</sub>H<sub>16</sub>Br<sub>2</sub>O: C, 36.04; H, 5.33; Br, 53.29. Found: C, 36.22; H, 5.42; Br, 52.40.

A mixture of 97.3 g. of the above bromo ketone with 100 ml. of purified<sup>17</sup> triethylamine in 600 ml. of purified<sup>18</sup> CHCl<sub>3</sub> was refluxed for 92 hr. The organic phase was extracted with three (discarded) 150-ml. portions of 3 N HCl, and then with two 75-ml. portions of 60% H<sub>2</sub>SO<sub>4</sub>. The latter were diluted to 1 l. and the cyclopropenone was extracted with CH<sub>2</sub>Cl<sub>2</sub>. Distillation afforded 4.1 g. (9.2%) of dipropylcyclopropenone, b.p. 66–68° (0.3 mm.), identical with authentic material (n.m.r. and infrared spectra).

The nonbasic organic material remaining in the CHCl<sub>3</sub> above was examined. Short-path distillation at 100° (2 mm.) separated it into 8.50 g. of distillable yellow liquid and 40.12 g. of dark brown residue. The volatile material showed a single main peak on v.p.c. analysis (phenyldiethanolamine column at 155°) and it was purified by preparative v.p.c. and identified as 4-methyl-5-propylcyclopentenone.

*Anal.* Calcd. for C<sub>9</sub>H<sub>14</sub>O: C, 78.21; H, 10.21. Found: C, 77.81; H, 10.32.

In the infrared the compound had peaks at 1715 and 1600 cm.<sup>-1</sup>. The ultraviolet spectrum (EtOH) showed  $\lambda_{\max}$  222 m $\mu$  (log  $\epsilon$  3.9). In the n.m.r. the compound had an apparent AB quartet at  $\tau$  2.3 (area 1)

(16) A. T. Blomquist and R. A. Vierling, *Tetrahedron Letters*, 655 (1961), report infrared bands at 1788, 1764, and 1611 cm.<sup>-1</sup> and in the ultraviolet  $\lambda_{\max}$  216 m $\mu$  ( $\epsilon$  18,800), 340 (26), and 355 (23) for dimethylcyclobutenedione.

(17) By distillation after treatment with phenyl isocyanate.

(18) Extracted with concentrated H<sub>2</sub>SO<sub>4</sub>, washed, dried, and distilled.

and 3.85 (area 1) with  $J_{AB} = 6$  c.p.s. and additional fine structure. There was a multiplet at  $\tau$  7.3 (area 1) and a complex set of peaks from 8.1 to 9.2 (area 10.8). The latter contained an apparent triplet at  $\tau$  9.1 ( $J = 5$  c.p.s.) and an apparent doublet at 8.75 ( $J = 7$  c.p.s.).

When unpurified CHCl<sub>3</sub> was used (contains ethanol as stabilizer) some ethyl 2-propylhex-2-enoate was also formed.

C. *Di-n-butylcyclopropenone.* Di-n-amyl ketone (56 g., 0.32 mole) was brominated with 110 g. (0.69 mole) of Br<sub>2</sub> in 500 ml. of CHCl<sub>3</sub> over 1.5 hr. Work-up with aqueous NaHSO<sub>3</sub>, then NaHCO<sub>3</sub>, followed by distillation afforded 80.2 g. (72%) of a dibromo ketone mixture, b.p. 101–106° (0.7 mm.).

*Anal.* Calcd. for C<sub>11</sub>H<sub>20</sub>Br<sub>2</sub>O: C, 40.27; H, 6.14; Br, 48.71. Found: C, 40.46; H, 6.41; Br, 48.42.

In the n.m.r. the mixture showed a major triplet at  $\tau$  5.45 ( $J = 7$  c.p.s.) and a minor triplet at 5.60 ( $J = 7$  c.p.s.) in a ratio of 5:1 with multiplets at 8.1, 8.85, and a triplet ( $J = 6$  c.p.s.) at 9.1. The relative areas of the four groups of peaks were 1:2.1:4.3:3.4.

This dibromo ketone (80 g.) was treated as above with 100 ml. of triethylamine in 700 ml. of CHCl<sub>3</sub>. Isolation of the cyclopropenone by use of 60% H<sub>2</sub>SO<sub>4</sub> gave 5.0 g. (12.4%) of di-n-butylcyclopropenone, b.p. 96–99° (0.4 mm.).

*Anal.* Calcd. for C<sub>11</sub>H<sub>18</sub>O: C, 79.46; H, 10.91. Found: C, 79.72; H, 11.27.

In the infrared the compound showed strong bands at 1850 and 1620 cm.<sup>-1</sup>. In the n.m.r. there was a triplet at  $\tau$  7.6 ( $J = 6$  c.p.s.), a multiplet centered at 8.6, and a triplet at 9.15 ( $J = 7$  c.p.s.); the ratio of areas was 1:2.3:1.7.

D. *Cycloheptenocyclopropenone.* 2,8-Dibromocyclooctanone, prepared according to the literature procedure,<sup>19</sup> had a two-proton triplet in the n.m.r. at  $\tau$  5.50 ( $J = 7$  c.p.s.), as expected. A mixture of 113.6 g. (0.4 mole) of this ketone and 161.9 g. (1.6 moles) of triethylamine in 500 ml. of CHCl<sub>3</sub> was heated for 48 hr. at 90° in a sealed tube under N<sub>2</sub>. The CHCl<sub>3</sub> solution was washed with water, then excess 2 N HCl, and then extracted with three 50-ml. portions of 75% H<sub>2</sub>SO<sub>4</sub>. These extracts were diluted with four parts of water and the cyclopropenone was extracted with two 100-ml. portions of CH<sub>2</sub>Cl<sub>2</sub>. After drying and solvent removal, distillation (under N<sub>2</sub>) afforded 27.7 g. (56%) of cycloheptenocyclopropenone, m.p. 44–51°. Purification by sublimation gave 25.1 g. (51%), m.p. 49–51°, raised to 52–53° on recrystallization.

*Anal.* Calcd. for C<sub>8</sub>H<sub>10</sub>O: C, 78.65; H, 8.25. Found: C, 78.85; H, 8.15.

In the infrared the compound showed peaks at 1840 and 1640 cm.<sup>-1</sup>. In the n.m.r. there was a four-proton triplet at  $\tau$  7.45 ( $J = 7$  c.p.s.) and a six-proton multiplet at 8.22.

E. *Cycloundecenocyclopropenone.* A solution of 102.0 g. (0.3 mole) of 2,12-dibromocyclododecanone<sup>20</sup> and 121.6 g. (1.2 mole) of triethylamine in 500 ml. of CHCl<sub>3</sub> was heated in a sealed tube under N<sub>2</sub> for 18 hr. Work-up as above (titration showed 96% Br<sup>-</sup> in the aqueous phase) afforded 4.25 g. (8%) of cycloundecenocyclopropenone, b.p. 120–124° (0.04 mm.), purified by

(19) G. Hesse and F. Urbanek, *Chem. Ber.*, **91**, 2733 (1958).

(20) W. Ziegenbein, *ibid.*, **94**, 2989 (1961).

careful extraction into 50 wt. % of H<sub>2</sub>SO<sub>4</sub> and distillation.

*Anal.* Calcd. for C<sub>12</sub>H<sub>18</sub>O: C, 80.85; H, 10.18. Found: C, 81.43; H, 10.28.

In the infrared, the compound showed peaks at 1830 and 1630 cm<sup>-1</sup>. The n.m.r. spectrum (neat, Me<sub>4</sub>Si internal standard) showed a triplet 2.75 p.p.m. downfield and a broad multiplet 1.45 p.p.m. downfield, with relative areas 4:13.4.

*F. Phenyl-diethylaminocyclopropenone.* Phenylacetone (13.4 g., 0.1 mole) was converted to a crude trichloro ketone, b.p. 110–112° (0.8 mm.), with SO<sub>2</sub>Cl<sub>2</sub> (45 g., 0.33 mole) in 100 ml. of acetic acid.

*Anal.* Calcd. for C<sub>9</sub>H<sub>7</sub>Cl<sub>3</sub>O: C, 45.51; H, 2.97; Cl, 44.78. Found: C, 44.42; H, 2.79; Cl, 44.05.

This ketone (9.04 g.) was added with stirring to an ice-cold solution of 6.05 g. of triethylamine and 2.50 g. of diethylamine in 250 ml. of CH<sub>2</sub>Cl<sub>2</sub> over 40 min. The CH<sub>2</sub>Cl<sub>2</sub> solution was washed with water and 2 *N* HCl, and weakly basic material was then isolated with 65% H<sub>2</sub>SO<sub>4</sub>. Chromatography on silica gel with CHCl<sub>3</sub>-ether, followed by distillation at 120–130° (0.001 mm.), yielded 0.20 g. of *diethylaminophenylcyclopropenone*.

*Anal.* Calcd. for C<sub>13</sub>H<sub>13</sub>NO: C, 77.58; H, 7.51; N, 6.95; mol. wt., 201. Found: C, 77.74; H, 7.68; N, 7.23; mol. wt. (osmometer), 194.

In the infrared, the compound absorbed at 1850 and 1630 cm<sup>-1</sup>. The n.m.r. spectrum showed a five-proton multiplet at  $\tau$  2.7, a pair of two-proton quartets near 6.7, and a pair of three-proton triplets near 8.8. The ultraviolet spectrum (EtOH) had  $\lambda_{\max}$  280 m $\mu$  ( $\epsilon$  27,000).

The compound was recovered unchanged on heating at 100° in concentrated H<sub>2</sub>SO<sub>4</sub> for 20 min., as well as from milder acid conditions. When the diethylamine was omitted from the above preparation no cyclopropenone derivatives could be isolated.

*G. Carbene Additions to Phenylmethoxyacetylene.* A mixture of 1.3 g. (0.01 mole) of phenylmethoxyacetylene<sup>21</sup> (contained in 2.0 g. of a mixture with methyl phenylacetate), 2.4 g. (0.0149 mole) of benzal chloride, and 3.4 g. (0.03 mole) of potassium *t*-butoxide in benzene was refluxed for 3 hr. The solution was washed with water and the product was chromatographed on silica gel to afford 0.745 g. (40%) of *diphenylcyclopropenone*,<sup>1b</sup> m.p. 114–117°.

A reaction between 2.0 g. of phenylmethoxyacetylene (0.015 mole, in 3.3 g. of the mixture with methyl phenylacetate) and 8.33 g. of sodium trichloroacetate (0.045 mole) in 30 ml. of dimethoxyethane was carried out at reflux for 24 hr. under N<sub>2</sub>. The resulting solution was quenched in water and extracted with ether to yield 5.57 g. of a dark oil with infrared absorptions at 1765 and 1720 cm<sup>-1</sup>. Careful distillation afforded 0.63 g. of impure *phenylmethoxydichlorocyclobutenone*.

*Anal.* Calcd. for C<sub>11</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>2</sub>: C, 54.37; H, 3.32. Found: C, 53.61; H, 3.80.

In the infrared the compound had a strong absorption at 1765 cm<sup>-1</sup>. In the n.m.r. it showed a two-proton multiplet at  $\tau$  2.52, a three-proton multiplet at 2.90, and a three-proton singlet at 5.58.

(21) T. L. Jacobs and W. R. Scott, *J. Am. Chem. Soc.*, **75**, 5497 (1953).

When 0.2 g. of the above dichloro ketone was dissolved in 0.5 ml. of concentrated H<sub>2</sub>SO<sub>4</sub>, HCl was evolved. After a few minutes at room temperature the solution was diluted with water, yielding 0.145 g. of *phenylmethoxycyclobutenedione*, m.p. 149–150° (lit.<sup>9</sup> 151–152.2°).

*Anal.* Calcd. for C<sub>11</sub>H<sub>8</sub>O<sub>3</sub>: C, 70.21; H, 4.29. Found: C, 70.42; H, 4.71.

The mass spectrum<sup>22</sup> showed major peaks at mass 188 and 160, with other fragments at 145, 132, 117, 89, 71, and 15. A peak at 189 had 12% of the size of the 188 peak. Hydrolysis of this methoxy ketone with warm H<sub>2</sub>SO<sub>4</sub> afforded *phenylhydroxycyclobutenedione*, m.p. 214° (lit.<sup>9</sup> 208–211°), which was also characterized by analysis and spectra.

2. *Reactions.* A. *Dipropylcyclopropenone.* Dipropylcyclopropenone (107 mg., 0.778 mmole) was heated under N<sub>2</sub> at 190–192° for 45 min. Quantitative infrared analysis after dilution showed that 60% of the cyclopropenone had decomposed. Quantitative v.p.c. analysis (Carbowax-1000, 78°) showed that 0.506 mmole of octyne-4 had been formed (65% conversion, 100% yield).

The basicity of dipropylcyclopropenone was determined by measuring the 60-Mc. n.m.r. spectrum of the ketone in aqueous H<sub>2</sub>SO<sub>4</sub> solutions. The chemical shift of the methyl group relative to the  $\alpha$ -CH<sub>2</sub> was 104.0 c.p.s. in dilute acid and 114.5 c.p.s. in 76.4% H<sub>2</sub>SO<sub>4</sub>. Eleven points were taken over an  $H_0$ <sup>23</sup> range of +0.25 to -6.35. A rough titration curve resulted whose midpoint, corresponding to 50% protonation, was at  $H_0 = -1.9 \pm 0.3$ .

Hydrogenation of dipropylcyclopropenone (0.941 g.) in 15 ml. of purified dioxane over 0.49 g. of pre-reduced PtO<sub>2</sub> was interrupted after uptake of 190 ml. (1 mole equiv.) of H<sub>2</sub>. The infrared spectrum showed the presence of unchanged starting material (strong bands at 1845 and 1637 cm<sup>-1</sup>) and two new bands at 1706 and 1686 cm<sup>-1</sup>. V.p.c. (5-ft. column, 20% Ucon polar on firebrick at 84°) showed three peaks with relative areas (flame ionization) of 1:7.5:1. The main component was isolated and identified as di-*n*-butyl ketone by comparison of infrared and mass spectra with those of an authentic sample. The minor components were identified as 2-propyl-2-hexenal and 2-propylhexanal from their v.p.c. retention times (*vide infra*).

Hydrogenation of dipropylcyclopropenone (1.300 g.) in 15 ml. of purified dioxane over 0.146 g. of Pd-C was monitored by examining aliquots in the infrared. After the absorption of 184 ml. of H<sub>2</sub> (0.715 mole equiv.) the infrared spectrum showed ca. 20% of starting material (1845 and 1637 cm<sup>-1</sup>) along with major absorption at 1686 cm<sup>-1</sup>. V.p.c. as above led to the same three peaks, but with relative areas 2.1:1:25. The major product, isolated by preparative v.p.c., was identified as 2-propyl-2-hexenal. In the infrared the compound had bands at 1686, 1635, and 2700 cm<sup>-1</sup>. The n.m.r. spectrum showed a singlet at  $\tau$  0.58 (area 1.28), a triplet at 3.55 ( $J = 7$  c.p.s.) (area 1.16), and broad multiplets at 7.70 (area 4.0) and at 8.55 and 9.00 (total area 10.6). The mass spectrum showed a strong parent ion at  $m/e$  140, as well as a reasonable fragmentation pattern.

(22) The compound was extensively characterized since it was our first example of a double expansion.

(23) M. Paul and F. Long, *Chem. Rev.*, **57**, 15 (1957).

The compound was converted to a red dinitrophenylhydrazone, m.p. 140–142° dec.

*Anal.* Calcd. for  $C_{15}H_{20}N_4O_4$ : C, 56.24; H, 6.29; N, 17.49. Found: C, 55.93; H, 6.29; N, 17.90.

The next largest v.p.c. peak was isolated and identified as 2-propylhexanal on the basis of air oxidation to the carboxylic acid, with infrared peaks at 1700 and 3500–2300  $cm^{-1}$  (broad) and a mass spectrum with ions at  $m/e$  158 ( $C_9H_{18}O_2$ )<sup>+</sup>, 116 ( $BuCH=C(OH)_2$ )<sup>+</sup>, 102 ( $PrCH=C(OH)_2$ )<sup>+</sup>, 73 ( $+CH_2-C=C(OH)_2$ ), and smaller fragments. The minor product was identified as di-*n*-butyl ketone by v.p.c. retention time.

*B. Cycloheptenocyclopropenone.* In an evacuated, sealed tube 3.66 g. (0.030 mole) of cycloheptenocyclopropenone was decomposed by immersion into a preheated oil bath at 250° for 30 min. On opening, the tube lost 0.40 g. (47% of theoretical, if CO; the CO was identified by infrared in a separate experiment); chromatography of the residue afforded 0.455 g. (16%) of triscycloheptenobenzene, m.p. 184–185°.

*Anal.* Calcd. for  $C_{21}H_{30}$ : C, 89.29; H, 10.71; mol. wt., 282. Found: C, 89.47; H, 10.48; mol. wt. (osmometer,  $CCl_4$ ), 279.

The infrared spectrum showed absorption at 2920, 2860, and 1450  $cm^{-1}$ . In the n.m.r. there was a broad peak at  $\tau$  7.30 and another at 8.45 in a ratio of 2:3. The ultraviolet spectrum (95% EtOH) had  $\lambda_{max}$  274  $m\mu$  ( $\epsilon$  262) and  $\lambda_{min}$  253  $m\mu$ .

When 2.44 g. (0.020 mole) of cycloheptenocyclopropenone and 7.69 g. (0.020 mole) of tetracyclone were heated in a sealed, evacuated tube at 250° for 30 min., chromatography on alumina afforded (with hexane) 50 mg. (2.7%) of triscycloheptenobenzene. Elution with  $CCl_4$  and benzene yielded 2.057 g. (22.8%) of 1,2-cyclohepteno-3,4,5,6-tetraphenylbenzene, m.p. 215–217°.

*Anal.* Calcd. for  $C_{35}H_{30}$ : C, 93.29; H, 6.71; mol. wt., 450. Found: C, 93.65; H, 6.51; mol. wt. (osmometer,  $CCl_4$ ), 435  $\pm$  15.

The ultraviolet spectrum (isooctane) had  $\lambda_{max}$  236  $m\mu$  ( $\epsilon$  42,000). The n.m.r. spectrum had peaks at

$\tau$  3.04 and 3.35 (20 protons), a multiplet at 7.35 (4 protons), and a multiplet at 8.30 (6 protons).

Elution with  $CH_2Cl_2$  yielded 1.624 g. (21% recovered) of tetracyclone. Elution with  $CHCl_3$  and ethyl acetate yielded 2.189 g. (21.5%) of a 1:1 adduct of tetracyclone with the cyclopropenone, m.p. 214–216°.

*Anal.* Calcd. for  $C_{37}H_{30}O_2$ : C, 87.71; H, 5.97; mol. wt., 507. Found: C, 87.35; H, 5.89; mol. wt. (osmometer,  $CCl_4$ ), 528.

In the infrared the compound had bands at 3080, 3058, 3030, 2925, 2855, 1763 (strong), 1670 (weak), 720, and 693  $cm^{-1}$ . The ultraviolet spectrum (EtOH) had  $\lambda_{max}$  345  $m\mu$  ( $\epsilon$  6900), 241 (30,000), and 206 (20,650), with a shoulder at 265. In the n.m.r., there was a multiplet at  $\tau$  3.01, one at 7.73, and a third at 8.49, with relative areas 43:8:12. The compound was recovered unchanged after 15 min. at 360°, or 14 hr. in refluxing (210°) nitrobenzene.

When 244 mg. of cycloheptenocyclopropenone was refluxed for 90 min. in 20 ml. of aqueous 10% KOH, 128 mg. (46%) of cycloheptene-1-carboxylic acid was obtained, m.p. 51–52°, identified by comparison with an authentic sample.<sup>24</sup> The n.m.r. spectrum had a one-proton triplet at  $\tau$  3 as well as signals in the aliphatic region.

*C. Cycloundecenocyclopropenone.* In an evacuated break-seal tube, 644 mg. of the cyclopropenone was kept for 30 min. at 210°. The gas was collected in an infrared cell, and it showed the typical CO peaks at 2165 and 2115  $cm^{-1}$ . The residue was filtered over  $Al_2O_3$  with pentane, and then distilled to yield 502 mg. (93%) of cycloundecyne,<sup>25</sup> b.p. 102–105° (12 mm.),  $n_D^{20}$  1.4876 (lit.  $n_D^{20}$  1.4875). The infrared spectrum was identical with that reported, and the n.m.r. spectrum showed a narrow peak at  $\tau$  8.49 and a broad one at 7.95 in a ratio of 14:4.

(24) E. A. Brande, W. F. Forces, and E. A. Evans, *J. Chem. Soc.*, 2202 (1953).

(25) V. Prelog and V. Boarlund, *Helv. Chim. Acta*, 38, 1776 (1955).

## Small-Ring Compounds. XLIII. Formolysis of Substituted Allylcarbinyl Tosylates<sup>1</sup>

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*Rate accelerations have been measured as a function of methyl substitution in 3- and 4-positions and phenyl substitution at the 4-position in the formolysis of allylcarbinyl tosylate. The largest factor,  $4.5 \times 10^3$ , was observed for ( $\gamma,\gamma$ -dimethylallyl)carbinyl tosylate. The nature of the solvolytic transition state is discussed; the results are shown to be inconsistent with formation of classical carbonium ion intermediates.*

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Numerous interconversion reactions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives have been reported in the last 2 decades.<sup>2</sup> In reactions where carbonium ion intermediates can quite reasonably be assumed, cyclopropylcarbinyl and cyclobutyl derivatives are highly reactive and yield very similar

(2) For a general introduction, see R. Breslow in "Molecular Rearrangements," P. deMayo, Ed., Interscience Publishers, New York, N. Y., 1963.