Addition of Cycloheptatrienylidene to cis- and trans-1,3-Pentadiene and to Styrene. Rearrangement of Spiro[2.6]nona-4,6,8-trienes¹

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Abstract: Cycloheptatrienylidene (1) adds to the terminal double bond of cis- and trans-1,3-pentadiene. The adduct from the cis diene, 1-cis-propenylspiro[2.6]nona-4,6,8-triene, rearranges above 50° to yield the geometric isomers of 8-methylbicyclo[5.4.0]undeca-1,3,5,9-tetraene (3a and 3b). 1-trans-Propenylspiro[2.6]nona-4,6,8-triene is unstable at room temperature and also rearranges to 3a and 3b, although giving different relative amounts. The carbene, 1, also adds to the vinyl group of styrene to yield 1-phenylspiro[2.6]nona-4,6,8-triene. At 75°, it rearranges to 8-phenylbicyclo[5.2.0]nona-1,3,5-triene. At temperatures above 135°, this bicyclic triene yields 2-phenylindan. The carbene additions are consistent with a nucleophilic attack by 1. Stepwise, diradical processes are suggested for the rearrangement of the spiro[2.6]nonatrienes.

ne of the atypical chemical properties of carbocyclic aromatic carbenes such as diphenylcyclopropenylidene and cycloheptatrienylidene (1) is their reluctance to add to simple olefins. For example, the



generation of cycloheptatrienylidene in the presence of cyclohexene, tetramethylethylene, or even norbornene gives no trace of adduct, the only product being the carbene dimer, heptafulvalene.² In fact, to date both diphenylcyclopropenylidene³ and 1² have been found to add only to double bonds substituted with strongly electron-withdrawing groups.

At this time we would like to report the addition of 1 to cis- and trans-1,3-pentadiene and styrene and the thermal rearrangements of the resulting spirononatrienes, one of which occurs at room temperature.⁴

Results

Cycloheptatrienylidene (1), generated by both thermolysis and photolysis of the sodium salt of tropone tosylhydrazone (2),² added in reasonable yield to both cis- and trans-1,3-pentadiene. For example, slow addition of 2.8 mmol of the salt to a solution of 35 mmol of trans-1,3-pentadiene in 20 ml of diglyme at 100° gave 5% heptafulvalene and 41% of a mixture of the geometric isomers of 8-methylbicyclo[5.4.0]undeca-1,3,5,9tetraene, 3a and 3b, in the ratio 88:12. Under the same conditions, the cis diene gave the same products although in different relative amounts, 3a:3b = 61:39.

Although the two adducts could not be separated by solution chromatography (tlc or column) and were unstable to preparative glpc conditions, it was possible by comparing the nmr spectrum of the product mixture

(1) Support for this work by the National Science Foundation is gratefully acknowledged.

(2) W. M. Jones and C. L. Ennis, J. Amer. Chem. Soc., 91, 6391 (1969). (3) W. M. Jones, M. E. Stowe, E. E. Wells, Jr., and E. W. Lester,

ibid., 90, 1849 (1968).

(4) Dr. K. Untch has also observed the addition of cycloheptatrienvlidene to styrene. We are indebted to Dr. Untch for communication of his results prior to publication and for many enlightening conversations.



from the trans diene with that from the cis diene to obtain the spectral data for the individual isomers. The methyl doublet in 3a was found at 1.24 ppm. The methine protons (H₇ and H₈) were found at 1.52 (t) and 2.5 (m), respectively. The methylene protons (H_{11}) were the most deshielded of the aliphatic protons, appearing at 2.99 ppm. The olefinic pattern was that expected for a 1,7-disubstituted cyclohepta-1,3,5-triene and inconsistent with a 7,7-disubstituted derivative. The nmr spectrum of 3b was very similar to that of 3a. The methyl group was located at slightly higher field, 1.11 ppm, but the remaining resonances were found in essentially the same positions as **3a** (see Experimental Section). Further support for the gross structures was obtained through double irradiation experiments (see Experimental Section). Unfortunately, it was not possible to assign the stereochemistry of **3a** and **3b** from the nmr spectra. Even nuclear Overhauser enhancement experiments designed to elucidate the relative distances between the methyl group and H_6 in **3a** and **3b** were not conclusive. The uv, ir, and mass spectra were all consistent with the assigned structures. Both adduct mixtures were reduced quantitatively over Pt/C with the uptake of 4 equiv of hydrogen.

The photolytic generation of cycloheptatrienylidene in the presence of trans-1,3-pentadiene at 28-31° again gave 3a and 3b albeit in reduced yield (ca. 15%, 3a:3b = 90:10). However, when the cis diene was used as the carbene trap, a new hydrocarbon, 1-cis-propenylspiro-[2.6]nona-4,6,8-triene (4), was isolated in 22% yield.



The structure of 4 was confirmed by its spectral properties (see Experimental Section). The cis configuration of the propenyl group is supported by the absence of a band near 960 cm⁻¹ in the ir.⁵ The allylic coupling constant between the methyl group and the olefinic proton (1.4 Hz) is of the magnitude expected for a trans allylic coupling.⁵ The adduct was totally reduced with 4 equiv of hydrogen.

Upon warming to 50-75°, 4 rearranged essentially quantitatively to a mixture of 3a and 3b (ratio, ca. 60:40). The rate data for this rearrangement are recorded in Table I.

Table I. Kinetic Data for the Rearrangement of 4 and 5

Start- ing ma- terial	$10^{4}k$, sec ⁻¹	Temp, °C	$\Delta H^{\pm},$ kcal/mol	ΔS^{\pm} , eu
4 4 4 5	$\begin{array}{c} 0.357 \pm 0.017^a \\ 1.53 \pm 0.07 \\ 5.61 \pm 0.16 \\ 0.724 \pm 0.077^b \end{array}$	50.25 62.69 75.18 74.90	24.0 ± 0.6°	$-4.8 \pm 1.5^{\circ}$

^a Uncertainties are standard deviations. ^b Followed through 1 half-life. ^c Uncertainties are statistical errors assigned by the method of E. L. Purlee, R. W. Taft, and C. A. Defazib, J. Amer. Chem. Soc., 77, 837 (1955).

Photolytically generated (30°) cycloheptatrienylidene also added to styrene to give 1-phenylspiro[2.6]nona-4-6,8-triene (5) in 28% yield.^{4,6} The structure of 5 is based on its spectral properties and reduction with 3 equiv of hydrogen to give 1-phenylspiro[2.6]nonane, which was prepared independently by two other methods.8 When 5 was heated in deuteriochloroform at 75° it was converted to 8-phenylbicyclo[5.2.0]nona-1,3,5-triene (6). Initially, the disappearance of 5 was





first order (nmr analysis, see Table I for rate data), but after 9 hr the ratio of 6:5 had leveled off at 85:15. This ratio was obtained in several experiments using different solvent systems. We feel that this is the thermodynamic equilibrium distribution even though pure 6 could not be obtained for equilibration. Attempts to separate 6 from 5 on Grade I alumina or preparative

(5) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1965.

(6) We have made use of this reaction in a Hammett study of the addition of 1 to substituted styrenes.7

(7) L. W. Christensen, E. E. Waali, and W. M. Jones, J. Amer. Chem. Soc., 94, 2118 (1972).

(8) K. Untch has used the thermolysis of cycloheptanone tosylhydrazone sodium salt in the presence of olefins to prepare spirononanes. We are indebted to Dr. Untch for communicating these results prior to publication.

glpc induced their conversion to 2-phenylindan, identified by comparing its infrared and nmr spectra with those reported in the literature.⁹ The structure of 6was evident from its spectral properties. The lack of any signal above 2.7 ppm (δ) showed all of the aliphatic protons to be either allylic or benzylic, eliminating the possibility that 6 was the 9-phenyl isomer. It is likely that 6 is a mixture of geometric isomers, since H_6 does not appear as a doublet of doublets, but a more complex multiplet. Heating 6 at 135° for 60 min resulted in the formation of 2-phenylindan.

As would be expected, the thermolysis of 2 in the presence of styrene gave a mixture of 5 and 6, their ratio decreasing with reaction time to a limiting value of 15:85, respectively.

Discussion

On the basis of its low reactivity with electron-rich double bonds² and its stereospecific addition to maleinitrile, 10 it has been previously concluded that cycloheptatrienylidene is a species which shows very low electrophilicity and adds to electron-deficient double bonds as a singlet in what is probably a concerted process. The results reported in this paper are consistent with the earlier conclusions in that initial formation of the spirononatrienes 4 and 5, despite the fact that they are thermodynamically less stable than their isomers 3 and 6, would be expected of a one-step addition of a singlet carbene. Furthermore, the low reactivity of the carbene with dienes and styrene as compared with dimethyl fumarate¹¹ as well as its specific attack on the less substituted double bond of pentadiene¹² are both consistent with (although the latter does not demand¹³) a relatively nucleophilic species.¹⁶

Both two-step and concerted mechanisms can be written for the conversion of 5 to 6. From orbital



symmetry considerations, an "allowed" concerted thermal rearrangement requires inversion at C₁.¹⁷ Inasmuch as this is sterically prohibited, either a "nonallowed" concerted ¹⁸ or a two-step process is indicated. Although it is not possible to choose between these two at this time, in view of the facility of the rearrangement which we believe to result from the inordinate stability

(9) G. Stanescu and M. Keul, Rev. Chim. (Bucharest), 13, 294 (1962); S. A. Galton, M. Kalafer, and R. M. Berlinger, J. Org. Chem., 35, 1 (1970).

(10) W. M. Jones, B. N. Hamon, R. C. Joines, and C. L. Ennis, Tetrahedron Lett., 3909 (1969).

(11) At 100° the carbene adds 50 times faster to dimethyl fumarate than to cis 1,3-pentadiene and at 31° it adds 80 times faster to the ester than to styrene: G. W. Killyon and E. E. Waali, unpublished results.

(12) None of the products that would result from addition to the more highly substituted double bond were detected.

(13) The preferred position of addition of electrophilic carbenes to dienes is apparently unsettled. For example, dichlorocarbene has been reported to show a slight preference for both the more¹⁴ and the less¹⁵ substituted double bonds of pentadiene. We are indebted to a referee for calling our attention to one¹⁵ of these references.

(14) L. Skattebol, J. Org. Chem., 29, 2951 (1964).
(15) P. Weyerstahl, D. Klamann, M. Fligge, C. Finger, F. Nerdel, and J. Buddrus, Justus Liebigs Ann. Chem., 710, 17 (1967).

(16) Addition of cycloheptatrienylidene to substituted styrenes has been found to give a ρ value of +1.05.7

(17) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970. (18) J. A. Berson and L. Salem, J. Amer. Chem. Soc., 94, 8917 (1972).

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of the tropenyl radical¹⁹ in conjunction with the stabilized benzyl radical,¹⁹ we tend to favor the two-step radical²⁰ process. Planned stereochemical studies will hopefully resolve this point.

The mechanism of the rearrangement of 4 to 3a and 3b (and presumably 8 to the same products) is even less obvious since in this case orbital symmetry considerations predict an "allowed" concerted suprafacial rearrangement.17 However, careful examination of molecular models shows that the "allowed" concerted rearrangement of 4 would lead only to the isomer of 3 in which H_7 and H_8 are cis to one another. Likewise, 8 would give rise to only the isomer of 3 which has H_7 and H_s trans. In fact, 4 gives both 3a and 3b in nearly equal amounts (61:39) and addition of the carbene to trans-1,3-pentadiene gives the same products although in different relative amounts (88:12). Based on the same arguments as those given above, but also with the same reservations, we tend once again to favor simple ring opening to a diradical as the first step in this rearrangement.²² A straightforward explanation for the difference in the rate of rearrangement of 4 and 8 can once again be found in an examination of molecular models. Thus, it can be seen that ring opening of 4 to give the planar allyl radical, 9, requires a transition state in which the methyl group is forced into opposition with either the cycloheptatriene ring or the methylene group of the cyclopropane ring. The trans isomer, 8, having no such restraint would, therefore, be expected to open to 10 more rapidly.



Assuming a diradical mechanism the rather remarkable facility of all of these rearrangements reemphasizes the elegantly demonstrated¹⁹ stability of the cycloheptatrienyl radical. This stability becomes even more impressive when it is recognized that a temperature of 350° is required to effect the conversion of **11** to indan (presumably through **12**).²⁴

Finally, it should be pointed out that a fused bicyclononatriene analog to 6 has been proposed^{2,25} as an

(19) G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, J. Amer. Chem. Soc., 91, 2823 (1969).

(20) It is, of course, also possible to write a two-step zwitterionic mechanism. However, the rate of rearrangement $(t_{1/2} = 160 \text{ min at } 75^\circ)$ compared with the dimethyl fumarate adduct of cycloheptatrienylidene (stable at $75^\circ)^2$ is only consistent with the diradical mechanism.²¹

(21) For relative stabilizing effect of phenyl and carbonyl on radicals, see K. D. King, D. W. Golden, and S. W. Benson, J. Amer. Chem. Soc., 92, 5541 (1970); and ref 19. For their effects on anions, see H. H. Jaffe, Chem. Rev., 53, 191 (1953).

(22) Although closure of either 9 or 10 can give both 3a and 3b, they would not be expected to give equal amounts of these two isomers. In fact, identical ratios of products would be expected only if 9 and 10 equilibrate before closure, an unlikely circumstance in view of the relatively high activation energy $(14-20 \text{ kcal/mol})^{23}$ for isomerization of allyl radicals.

(23) D. M. Golden, Int. J. Chem. Kinet., 1, 127 (1969); R. J. Crawford, J. Hamelin, and B. Strehlke, J. Amer. Chem. Soc., 93, 3811 (1971).
(24) D. Schonleber, Chem. Ber., 102, 1789 (1969).



intermediate for the conversion of 9 to the indan 13.2.26



To the best of our knowledge, isolation of 6 and its thermal rearrangement to 2-phenylindan constitutes the first direct evidence for the bicyclononatriene intermediate in this type of reorganization.

Experimental Section

General. Melting and boiling points are uncorrected. Infrared spectra were recorded on a Beckmann Model IR10 and are reported in units of cm⁻¹. Nuclear magnetic resonance spectra were determined using a Varian A-60A or XL-100 using tetramethylsilane as an internal standard. Chemical shifts are reported in the δ scale. Uv spectra were run on a Cary Model 15 spectrometer using 1-cm quartz cells. The analytical glpc was performed on a Varian Aerograph Model 1200 instrument equipped with 1/s in. columns and a flame ionization detector. The preparative glpc was accomplished on a Varian Aerograph Model A-90P with a thermal conductivity detector. Mass spectra were determined using a Hitachi-Perkin-Elmer RMU-6E instrument with an ionizing voltage of 70 eV. The elemental analyses were performed by Atlantic Microlab, Atlanta, Ga.

The sodium salt of tropone tosylhydrazone (2) was prepared as previously reported.² Reagent grade diglyme and tetrahydrofuran were distilled from lithium aluminum hydride for the purpose of drying. Styrene was distilled at reduced pressure before use. *cis*-and *trans*-1,3-pentadiene (PCR, Inc., greater than 99% geometric purity) were also distilled before use.

Thermolysis of Tropone Tosylhydrazone Sodium Salt (2) in the Presence of trans-1,3-Pentadiene. A solution of 20 ml of dry diglyme and 2.5 g (35 mmol) of trans-1,3-pentadiene was heated to 100° . Over a 40-min period, 0.82 g (2.8 mmol) of 2 was added. After an additional 50 min, the mixture was cooled and added to 150 ml of water. The organic material was extracted with three 25-ml portions of pentane. The combined pentane extracts were washed with two portions of water and dried over anhydrous MgSO₄. Glpc analysis showed that there was no cis-trans isomerization of the diene during the thermolysis. After the solution was filtered, the pentane and excess diene were removed under vacuum. The residue was chromatographed over alumina (Woelm, grade III, basic) using pentane as the eluent. The geometric isomers of 8-methylbicyclo[5.4.0]undeca-1,3,5,9-tetraene (3a and 3b, 180 mg, 41%) preceded heptafulvalene (13 mg, 5%). Analytical glpc (SE-30, 70°) showed the presence of 88% 3a and 12% 3b. Under preparative glpc conditions, the material underwent rearrangement or decomposition as evidenced by the collection of aromatic compounds with 3a and 3b. The mixture showed only one spot upon thin-layer chromatography (silica gel, pentane). Due to the predominance of 3a in the mixture, its spectral characteristics could be reasonably established.

(25) T. Mukai, T. Nakazawa, and K. Isobe, Tetrahedron Lett., 565 (1968).

(26) An intermediate similar to 6 has also been proposed to explain the products resulting from the addition of carbethoxycarbene to biphenylene.²⁷

(27) A. S. Kende and P. T. MacGregor, J. Amer. Chem. Soc., 86, 2088 (1964).

3a: nmr (CDCl₃) δ 1.24 (d, J = 7.3 Hz, 3, methyl), 1.52 (t, J = 6 Hz, 1, C₇ methine), 2.5 (m, 1, C₈ methine), 2.99 (m, 2, methylene), 4.94 (d of d, J = 8.9 and 6.0 Hz, 1, H₆), 5.85 and 6.1 (both m, 4, H₂, H₅, H₀, H₁₀), 6.55 (asym t, 2, H₃, H₄). Irradiation of the resonance at 2.5 ppm (H₈) collapsed the methyl signal to a singlet while the resonance at 1.52 (H₇) became a doublet (6 Hz). Saturation of the triplet at 1.52 (H₇) collapsed the signal at 4.94 to a doublet (8.9 Hz). Irradiation throughout the olefinic region had no effect on the methyl doublet; ir (neat) 3040 (s), 3025 (s), 2970 (s), 2870 (m), 2850 (m), 1640 (w), 1620 (w), 1460 (m), 1385 (m), 684 (m), 732 (s), 715 (s); uv max (*n*-heptane) 264 nm (ϵ 3110); mass spectrum *m*/*e* (rel intensity), 158 (43), 143 (98), 129 (57), 128 (100), 115 (44). A satisfactory analysis could not be obtained due to oxidation, although the C/H ratio was proper.

The mixture of 3a and 3b was reduced over 5% platinum on charcoal in ethanol with the uptake of 4.1 equiv of hydrogen. This mixture of reduced adducts (three isomers observed by glpc) was purified in concert by preparative glpc: nmr (CDCl₃) 0.86 (d, J = 6.5 Hz, 3, methyl), 0.9 to 1.9 (broad m, 19, everything else).

Anal. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 86.50; H, 13.27.

Thermolysis of 2 in the Presence of *cis*-1,3-Pentadiene. In a procedure identical with that described above, a mixture of 20 ml of diglyme, 35 mmol of *cis*-1,3-pentadiene, and 3.4 mmol of 2 was heated at 100° . Isomerization of the cis diene to the trans diene did not occur under the reaction conditions (glpc analysis). Workup was identical with that described above. Glpc analysis of this mixture (0.198 g, 38% yield) showed it to be 61% 3a and 39% 3b. By comparison of the spectral properties of this mixture with the mixture derived from the trans diene, the following spectral properties of 3b were inferred.

3b: nmr (CDCl₃) δ 1.11 (d, J = 6.5 Hz, methyl), 1.6 (m, H₇), 2.5 (m, H₈), 2.94 (m, methylene), 5.01 (d of d, J = 6 and 9 Hz, H₆), 5.7-6.2 (m, H₂, H₅, H₉, H₁₀), 6.54 (asym t, H₈, H₄); ir (neat) essentially same as **3a**; mass spectrum m/e (rel intensity) 158 (50), 143 (100), 129 (68), 128 (91), 115 (42). Oxidation precluded a satisfactory elemental analysis.

This mixture was likewise reduced (5% Pt/C in ethanol) with the consumption of 3.9 equiv of hydrogen. The reduced adduct mixture had essentially the same nmr spectrum as that found above: nmr (CDCl₃) δ 0.86 (d, J = 6.5 Hz, 3, methyl), 0.9 to 1.9 (broad m, 19, everything else).

Anal. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 86.58; H, 13.25.

Photolysis of 2 in the Presence of *trans*-1,3-Pentadiene. To a vigorously stirred mixture of 6.8 g (100 mmol) of *trans*-1,3-pentadiene and 15 ml of dry tetrahydrofuran was slowly added 0.8 g (2.8 mmol) of 2 while irradiating the mixture through Pyrex using a 550-W Hanovia medium-pressure mercury lamp. The temperature was maintained at $28-31^{\circ}$. The addition time was 3 hr. After 6 additional hr of photolysis time, the reaction mixture was worked up as in the thermolysis experiments (see above). Only **3a** and **3b** were observed (*ca*. 15% yield, nmr analysis) in the ratio of *ca*. 90:10 with about 10% heptafulvalene.

Photolysis of 2 in the Presence of *cis*-1,3-Pentadiene. The photolysis and work-up procedure here was the same as for the trans diene. The photolysis was conducted at 31° . From 1.0 g of 2, 6.8 g of *cis*-1,3-pentadiene, and 10 ml of tetrahydrofuran resulted 0.114 g of 1-*cis*-propenylspiro[2.6]nona-4,6,8-triene (4, 21% yield) and 10% heptafulvalene. A satisfactory elemental analysis could not be obtained due to oxidation.

4: nmr (CDCl₃) δ 0.60 (d of d, J = 4.1 and 6.7 Hz, 1, trans-H₂), 0.95 to 1.45 (m, 2, H₁ and cis-H₂), 1.61 (d of d, J = 7.5 and 1.4 Hz, 3, allylic methyl), 4.7–5.5 (m, 4, propenyl olefinic, H₄, H₉), 5.8–6.5 (m, 4, H₃, H₆, H₇, H₈); ir (neat) 3010 (s), 1035 (w), 700 (s); mass spectrum *m/e* (rel intensity) 158 (59), 143 (100), 129 (58), 128 (96), 115 (56).

A sample of 4 was hydrogenated over 5% Pt on C in ethanol with the consumption of 4 equiv of hydrogen. The reduced material was collected by preparative glpc. From the nmr spectrum it appears that rearrangement (but not hydrogenolysis) has occurred since it lacks cyclopropyl hydrogens: nmr (CDCl₃) 2.0–0.8 ppm (m); mass spectrum m/e (rel intensity) 166 (33), 123 (37), 96 (36), 95 (49), 82 (43), 81 (100), 67 (59), 55 (47).

Anal. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 86.65; H, 13.28.

Photolysis of 2 in the Presence of Styrene. The above photolysis and work-up procedure was used. If any styrene was present after chromatography, it was removed at 0.5 mm. From 0.58 g (1.96

mmol) of **2**, 10 ml (87 mmol) of styrene, and 10 ml of pentane was isolated 0.138 g (0.71 mmol) of 1-phenylspiro[2.6]nona-4,6,8-triene (**5**, 28%). **5**: nmr (CDCl₃) δ 1.21 (overlapping d, J = 8.0 and 7.3 Hz, 2, cyclopropyl methylene), 2.10 (t, J = 7.6 Hz, 1, cyclopropyl methine), 5.00 and 5.35 (both d, both J = 9.5 Hz, 1 each, H₄ and H₆), 5.9–6.5 (m, 4, H₅, H₆, H₇, H₈), 7.1 (m, 5, aromatic); ir (neat) 3080 (w), 3055 (w), 3010 (s), 1601 (m), 1495 (m), 1451 (m), 909 (s), 776 (m), 732 (s), 697 (s); mass spectrum *m/e* (rel intensity) 194 (2), 121 (10), 119 (11), 86 (97), 84 (100). A satisfactory analysis could not be obtained due to oxidation.

The reduction of **5** over platinum on charcoal in ethanol with the consumption of 3 equiv of hydrogen gave 1-phenylspiro[2.6]nonane which was identical with that prepared by two different alternate methods (see below).

8-Phenylbicyclo[5.4.0]nona-1,3,5-triene (6). Heating a sealed, degassed nmr solution of 5 in $CDCl_3/TMS$ at 75° resulted in the conversion of 5 to 6. After 9 hr, the composition was 85% 6 and 15% 5 which did not change with time. Chromatography of this mixture over activity grade I basic alumina with pentane resulted in its complete conversion to 2-phenylindan. The ir and nmr spectral properties of 2-phenylindan were identical with those previously reported.⁹ If a mixture of 5 and 6 was heated at 135° for 1 hr, it was converted to 2-phenylindan. Preparative glpc also effected the rearrangement.

6: nmr (CDCl₃) δ 2.7–4.0 (m, 4, aliphatic), 4.9–5.4 (m, 1, H₆), 5.6–6.2 (m, 4, H₂, H₃, H₄, H₆), 7.25 (m, 5, aromatic); ir (neat) 3080 (w), 3060 (w), 3020 (s), 1602 (m), 1493 (m), 1401 (m), 749 (s), 698 (s); mass spectrum *m/e* (rel intensity) 194 (88), 179 (100), 178 (46), 116 (65), 106 (45), 105 (46), 78 (52), 77 (55).

A sample of 6 (containing 15% 5) was reduced over platinum/ charcoal in ethanol with the consumption of 3 equiv of hydrogen (four isomers are possible, three were seen by glpc). Separation of this mixture from 1-phenylspiro[2.6]nonane was achieved by preparative glpc: nmr (neat with external TMS) δ 6.81 (s, 5, aromatic), 2.9–0.7 (m, 15, aliphatic); mass spectrum m/e (rel intensity) 200 (10), 117 (11), 105 (13), 104 (100), 92 (11).

Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.81; H, 10.10.

Thermolysis of 2 in the Presence of Styrene. The above thermolysis procedure was used with styrene as the trapping material. From 0.97 g (3.28 mmol) of 2, 4.0 ml (35 mmol) of styrene, and 30 ml of diglyme was isolated (chromatography over grade III, basic alumina with *n*-pentane) 0.235 g (47%) of a mixture of 5 and 6 in the ratio 15:85, when the total reaction time was 180 min. If the reaction time was reduced to 90 min, the ratio was 21:79. With a 35-min reaction time, the ratio was 46:54.

1-Phenylspiro[2.6]nonane. a. From Benzylidenecycloheptane. A mixture of 15.4 g (0.226 mol) of sodium ethoxide, 87.6 g (0.226 mol) of benzyltriphenylphosphonium chloride,28 and 25.0 g (0.223 mol) of cycloheptanone in 250 ml of absolute ethanol was heated at 70° for 11 hr. The mixture was cooled and filtered. Most of the ethanol was removed under vacuum. The remaining solid was extracted with generous amounts of pentane The pentane extracts were concentrated under vacuum and the residue was vacuum distilled. Benzylidenecycloheptane distilled at 115-119° (3.5 mm): nmr (CCl₄) δ 1.60 (m, 8, methylene protons at C₃ through C₆), 2.4 (m, 4, allylic methylene), 6.23 (narrow m, 1, olefinic), 7.14 (s, 5, aromatic); ir (neat) 3080 (m), 3050 (m), 3010 (m), 2910 (s), 2850 (s), 1640 (w), 1600 (m), 1495 (m), 1445 (s), 920 (m), 752 (s), 699 (s); uv max (*n*-hexane) 250 nm ($\epsilon 1.52 \times 10^4$); mass spectrum m/e (rel intensity) 186 (83), 170 (35), 129 (56), 115 (40), 105 (100). 95 (69), 91 (56)

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.11; H, 9.76.

A zinc-copper couple (10.5 g) was prepared in ether by the method of Le Goff.²⁹ This was treated with 15.0 g of benzylidenecycloheptane and 30.3 g of methylene iodide and brought to reflux for 21 hr. After acidification and aqueous work-up with pentane extraction, a residue was obtained which was 30% 1-phenylspiro-[2.6]nonane and 70% starting material. The spiro compound was isolated by preparative glpc: nmr δ 0.6–1.0 (m, 2, cyclopropyl methylene), 1.1–1.7 (m, 12, cycloheptyl protons), 1.90 (d of d, J = 8.5 and 6.0 Hz, 1, methine), 7.19 (s, 5, aromatic); ir (neat) 3055 (m), 3020 (m), 2995 (m), 2920 (s), 2850 (s), 1602 (m), 1495 (m), 1450 (m), 698 (s).

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Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.96; H, 10.00.

b. From Cycloheptanone Tosylhydrazone Sodium Salt and Styrene. A mixture of 1.0 g (3.4 mmol) of cycloheptanone tosylhydrazone sodium salt, 4.5 g (43 mmol) of styrene, and 30 ml of diglyme was heated at 125° for 1 hr. After cooling, the mixture was added to 150 ml of water and extracted with three 25-ml portions of pentane. The pentane extracts were concentrated and the excess styrene was removed under vacuum at 0.5 mm. The residue was then chromatographed over alumina (grade III, basic, pentane). The yield of 1-phenylspiro[2.6]nonane was 0.45 g (67%). This sample was identical with that prepared above. **Rearrangement Rates of 4 and 5.** A solution of 4 or 5 (0.10 g) was dissolved in 1.3 ml of CDCl₃ containing 1% TMS. The solution was divided and placed into three nmr tubes. These solutions were then degassed (at least five freeze-pump-thaw cycles each) and sealed under vacuum. They were heated in a water bath whose temperature was controlled to 0.05°. At intervals, a tube was removed and quenched in ice-water. An nmr spectrum was obtained. The relative concentration of 4 or 5 was determined by integrating the signal at 0.60 or 1.21 ppm, respectively, vs. the internal standard, TMS. The ratio of 4 or 5 to TMS could be determined with a reproducibility of ca. 4%. The kinetic data are in Table I. The rate constants were determined by a least-squares method.

Mechanism of Reaction of Carbon Monoxide with Phenyllithium¹

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Abstract: The product mixtures obtained by reaction between phenyllithium and carbon monoxide in diethyl ether, followed by hydrolysis, include benzophenone (1), α, α -diphenylacetophenone (2), benzil (3), α, α -diphenyl- α -hydroxyacetophenone (4), benzpinacol (5), α -hydroxyacetophenone (6), 1,3,3-triphenylpropane-1,2-dione (7), 1,3,3-triphenylpropan-1-one-2,3-diol (8), and benzhydrol (9). Compounds 1, 2, 6, 7, and 8 are produced in significant yields; 3, 4, 5, and 9 are produced in trace quantities. Spectroscopic studies establish dilithium benzophenone dianion (18) as the first long-lived intermediate formed in this reaction; qualitative correlations between the basicity of a number of organolithium reagents and their reactivity toward carbon monoxide suggests, but does not prove, that benzoyllithium is a precursor of 18. Labeling experiments indicate that the products ultimately isolated following hydrolysis of the reaction mixture are derived from at least two pathways which compete for the initially formed 18. One involves combination of 18 with 1 equiv of phenyllithium and 1 equiv of carbon monoxide, followed by elimination of 1 equiv of lithium oxide, yielding 17, the lithium enolate of 2; a second involves combination of 18 with 1 equiv of phenyllithium and 2 equiv of carbon monoxide, yielding 22, the trilithium trianion of 8. Hydrolysis of 17 yields 2 directly. Hydrolysis of 22 yields 8; reverse aldol reactions involving 8 or its precursors generate 1 and 6. The mechanism proposed to account for the major products of the reaction of phenyllithium and carbon monoxide is outlined in Scheme III. On the basis of this scheme, plausible paths to the minor products of the reaction are proposed.

The addition of nucleophiles to carbon monoxide, activated by coordination to metal ions, forms the basis for a thoroughly explored and useful class of reactions. Transformations related to the hydroformylation process,⁴ additions of organolithium reagents to metal carbonyls,⁵ carbonylation of mercury(II) salts,⁶ organoboranes,⁷ and organocopper reagents,⁸ metal-

(1) Supported by the National Institutes of Health, Grants GM 16020 and HL-15029, and by the U. S. Army Research Office (Durham), Grant ARO-D-31-124-G69.

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catalyzed oxidative coupling of amines with carbon monoxide,⁹ and metal-catalyzed oxidation of carbon monoxide in aqueous solution,¹⁰ each involve the attack of formally anionic groups on metal-coordinated carbon monoxide. Acylmetallic compounds have either been inferred or identified as intermediates in many of these reactions, and this class of substance provides the foundation for discussions of their mechanisms.^{4,5}

The reactions of nucleophiles with free or weakly coordinated carbon monoxide are less well understood. Base-catalyzed carbonylation of alcohols and amines.^{11,12} and the reactions of organolithium,¹³

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