tion of chemicals. Melting points and boiling points are uncorrected.

Materials. *n*-Pentane and cyclohexane (Fisher Scientific Co., Spectrograde) were used without further purification. Naphthalene (Baker Analyzed Reagent) was zone refined. Michler's ketone and *p*-phenylbenzophenone (Eastman Organic Chemical Co.) were recrystallized from ethanol with mp 171–172 and 101–102°, respectively. Isoprene (Aldrich Chemical Co., puriss), 1,3-cyclohexadiene, 2,5-dimethyl-2,4-hexadiene (Aldrich Chemical Co.), and 2,3-dimethyl-1,3-butadiene (Chemical Samples Co.) were purified by distillation from lithium aluminum hydride prior to use. *cis,cis*-Cyclooctadiene (Chemical Samples Co.) was eluted through a 5-cm neutral alumina column and distilled. *cis,trans*-1,3-Cyclooctadiene was prepared by the benzophenone-photosensitized reaction of *cis,cis*-1,3-cyclooctadiene following the method of Liu.[25] The material was stored at −77° to prevent dimerization. Bicyclo[4.2.0]oct-7-ene was prepared by a photosensitized reaction of *cis,cis*-1,3-cyclooctadiene at the boiling point of cyclohexane following the method of Liu.[25] *cis*-Cyclooctene (Columbian Carbon Co.) was purified on a preparative gc with an 80 in. × 0.75 in. 20% of SE-30 on Chromosorb W (30–60 mesh) column. *trans*-Cyclooctene was synthesized from cyclooctylamine (Aldrich Chemical Co.) by the method of Cope[35] and purified under the same conditions as described for the cis isomer. 1,2-Dimethylcyclobutene was prepared following a modified version of Crowley's method.[36] A 1% solution of 2,3-dimethyl-1,3-butadiene (Chemical Samples Co) in pentane was irradiated under nitrogen by using a Hanovia 450-W mercury lamp with a Vycor filter. The reaction was monitored on a Varian A-90-P gas chromatograph with a 20 ft × 0.25 in. 20% β,β'-oxydipropionitrile on Chromosorb W column (column temperature at 25°). The reaction was stopped when the amount of starting material ceased to diminish. *n*-Pentane was distilled off on a 16 in. spinning band column. The concentrated solution was treated with maleic anhydride in ether to remove the unreacted diene. The solution was washed thoroughly with aqueous sodium bicarbonate solution and then water. After the solution was dried over anhydrous sodium sulfate, the fractions were collected by spinning band column distillation. The boiling point is 68–69°, and the glc analysis showed no more than 0.01% 2,4-dimethyl-1,3-butadiene remained.

Fluorimetry. Relative fluorescence intensities measurements were made on a Perkin-Elmer constant energy fluorimeter at least twice for each sample. The instrument was modified to accept liquid samples by rotating it 90° from its normal position. Sample solutions (3 ml) in 13-mm Pyrex tubes were degassed by three freeze–pump–thaw cycles to 5×10^{-4} mm.

Quantum Yields. Samples for irradiation were held in a modified version of Merry-Go-Around[26,37] with a 450-W mercury lamp as a light source. A filter solution containing 0.023% K_2CrO_4 and 0.1% NaOH which was circulated through a quartz dipper well (path length 0.44 cm) and a Corning 7-54 filter were combined to isolate the 313-nm mercury line. Ferrioxalate actinometry was used for measuring light intensities.[26,38] All product analyses after irradiation were performed by gas chromatography.

Adducts were prepared by irradiating sample tubes containing 0.234 *M* naphthalene and 0.445 *M cis,trans*-1,3-cyclooctadiene for a period such that at least a 50% conversion occurred. The mixture was then purified by preparative tlc and glc (2 ft × 0.25 in. 20% SE-30 on Chromosorb W as column at 190°). Three fractions were collected by glc with retention time 10.9, 13.7, and 16.3 min, respectively. Nmr spectra (CCl_4) for fraction 1 (R_t = 10.9 min) showed a broad singlet at τ 3.2 (4 H), a multiplet around 3.4–4.2 (2 H), and multiplets at 4.5–5.4 (2 H), 6.3–6.9 (2 H), 7.5–9.0 (10 H); fraction 2 (R_t = 13.7 min) showed a broad singlet at τ 3.12 (4 H), multiplets at 3.9 (1 H), 4.0–5.0 (2 H), 6.0–6.3 (1 H), 6.5–7.0 (2 H), 7.5–9.0 (10 H); fraction 3 (R_t = 16.3 min) showed a broad singlet at τ 3.25 (4 w), and multiplets at 3.6–5.0 (4 H), 6.4–7.2 (2 H), 7.2–9.5 (22 H). The nmr for fraction 3 could indicate a 1:2 naphthalene-*N*-**1** adduct, however, mass spectra showed peaks at *m/e* 236 (parent peak, 1:1 adduct), 128 (major peak, napthalene), and 108 (1,3-cyclooctadiene) for all three fractions. The peak at *m/e* 344 (parent peak for 1:2 napthalene–**1** adduct) was searched for carefully without any success.

Acknowledgment. The authors gratefully thank the Research Corporation for a Frederick Gardner Cottrell Grant and the Research Foundation of the State University of New York for a Grant-in-Aid.

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(35) A. C. Cope and R. B. Bach, *Org. Syn.*, **49**, 39 (1969).

(36) K. J. Crowley, *Tetrahedron*, 1001 (1965).

(37) M. G. Moses, R. S. H. Liu, and B. M. Monroe, *J. Mol. Photochem.*, **1**, 245 (1969).

(38) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

Formation and Study of the α Monoanion and α,α' Dianion of 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one[1]

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Contribution from the Department of Chemistry, Western Michigan University, Kalamazoo, Michigan 49001, and Research Laboratories, The Upjohn Company, Kalamazoo, Michigan 49001. *Received December 18, 1972*

Abstract: 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (**7**) has been converted to its monoanion **8** and its dianion **9**. It was found that the negative charge in dianion **9** was delocalized not only into the carbonyl group and the two phenyl rings, but also into the carbon–carbon double bond at $C_{6,7}$, thereby making the 2,4-diphenylbicyclooctenone dianion **9** the first homoaromatic analog of the six π-electron aromatic cyclopentenone dianion **6**. Monoanion **8** was found to exist as a mixture of two isomeric enolates **8a** and **8b** in a ratio of 2:1, respectively. This ratio was shown to be solvent independent. It was further established that there was no interaction between the negative charge at C_2 and the $C_{6,7}$ olefinic group in either isomer. Rationalizations are offered for these observations, and the properties of the 2,4-diphenylbicyclooctenone enolate monoanions **8a,b** are compared and contrasted with those of the enolates derived from simple 2,6-disubstituted cyclohexanones.

The stabilization of carbanions and carbonium ions by means of cyclic charge delocalization or aromaticity is well documented[3] and universally accepted. The cyclopentadienyl anion[4] **1** and the cyclopropenyl

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(1) Taken largely from the M. A. dissertation of E. W. Crowe, Western Michigan University, 1972.

(2) (a) Western Michigan University; (b) The Upjohn Co.

(3) (a) G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, London, 1969, pp 71–109; (b) R. C. Haddon, V. R. Haddon, and L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy of Annulenes," Springer-Verlag, New York, N. Y., 1971, pp 190–200.

(4) (a) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963); (b) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Amer. Chem. Soc.*, **82**, 5846 (1960); (c) J. R. Leto, F. A. Cotton, and J. S. Waugh, *Nature (London)*, **180**, 978 (1957).

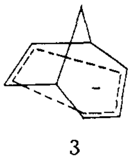
cation[5] **2** are just two examples of a large number of

1

2

well-known carbanions and carbonium ions whose unusual stability is thought to be due to the above effect.

During the past 15 years a large body of evidence has been presented in support of a new stabilization mechanism for carbanions and carbonium ions, generally known as homoaromaticity.[6] Homoaromaticity involves stabilization by means of cyclic electron delocalization across intervening carbon atoms. In aromaticity cyclic electron delocalization takes place over adjacent carbon atoms. Thus, the bicyclooctadienyl anion[7] **3** and the 7-norbornenyl cation[8] **4** are considered to be homologs of **1** and **2**, respectively, and their unusual stability has been attributed to homoaromaticity.



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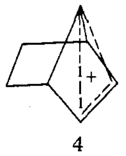

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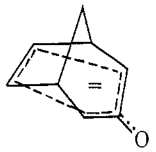
Conceptually, the homo relationship between the bicyclooctadienyl anion **3** and the cyclopentadienyl anion **1** may be extended to a number of other systems, not necessarily monoanions, which contain the proper number of π electrons. For example, dianion **5** may be regarded as a bishomoaromatic analog of the well-known aromatic cyclopentenone dianion[9] **6**.



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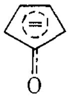

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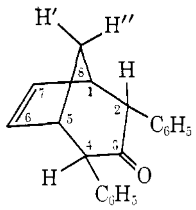
The purpose of the present investigation was to examine the feasibility of this concept. For this purpose, 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one[10,11] (**7**) was converted to its dianion **9**, and the properties of this intermediate were closely studied, in order to examine the possibility of long-range interactions between the negative charges at $C_{2,4}$ and the olefinic group at $C_{6,7}$.



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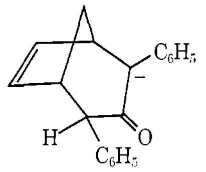

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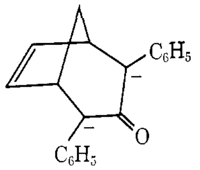

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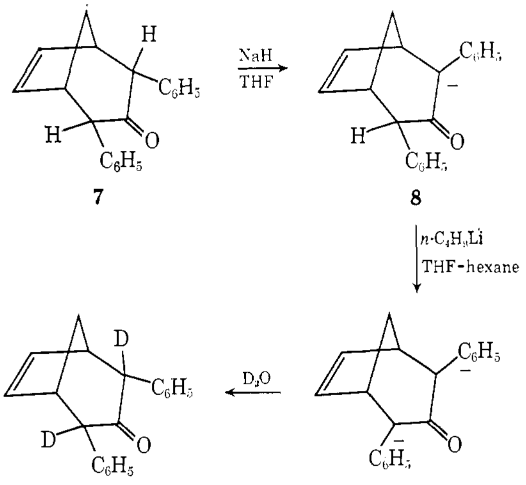
In addition, the possibility of long-range interactions in monoanion **8** was investigated. Such interactions would lead to a homoallylic enolate anion.

Finally, since monoanion **8** was actually found to exist in two isomeric forms, **8a** and **8b**, the nature of the configurational composition of the mixture has been examined, and arguments are presented in order to explain the observed results.

Results and Discussion

Preparation and Properties of 2,4-Diphenylbicyclo-[3.2.1]oct-6-en-3-one Dianion (9). The brick-red dianion **9** was obtained from 2,4-diphenylbicyclo[3.2.1]-oct-6-en-3-one[10] (**7**) in practically quantitative yield by means of a two-step process first reported by Hauser[12] and his coworkers in 1967. This process involved initial treatment of bicyclic ketone **7** with excess sodium hydride in tetrahydrofuran (THF) or THF-d_8 to give enolate monoanion **8**, which was subsequently reacted with *n*-butyllithium to produce dianion **9** (Scheme I).

Scheme I



The advantage of the two-step process over direct treatment of the bicyclic ketone **7** with *n*-butyllithium lies in the fact that initial monoanion formation by means of sodium hydride deactivates the carbonyl group, thereby nullifying its subsequent attack by the organolithium reagent.[12]

Evidence supporting the presence of monoanion **8** is presented in the next section. The presence of dianion **9** was ascertained by direct examination of the reaction mixture by nmr, and by quenching the dianion solution with deuterium oxide to give 2,4-dideuterated ketone **7**-d_2 (Scheme I).

The nmr spectrum of dianion **9** in THF-d_8–hexane was recorded on a Varian XL-100 instrument using

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(5) (a) R. Breslow, J. T. Groves, and G. Ryan, *J. Amer. Chem. Soc.*, **89**, 5048 (1967); (b) D. G. Farnum, G. Mehta, and R. G. Silberman, *ibid.*, **89**, 5048 (1967); (c) G. A. Olah, J. M. Bollinger, and A. M. White, *ibid.*, **91**, 3667 (1969).

(6) (a) S. Winstein, *J. Amer. Chem. Soc.*, **81**, 6524 (1959); (b) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

(7) (a) J. M. Brown and J. L. Occolowitz, *Chem. Commun.*, 376 (1969); (b) S. Winstein, M. Ogliaruso, M. Sakai, and J. M. Nicholson, *J. Amer. Chem. Soc.*, **89**, 3656 (1967); (c) J. M. Brown and J. L. Occolowitz, *J. Chem. Soc. B*, 411 (1968).

(8) (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955); (b) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); (c) S. Winstein, A. L. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963); (d) M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3185 (1966); (e) H. G. Richey, Jr., and R. K. Lustgarten, *ibid.*, **88**, 3136 (1966).

(9) R. E. Benson and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **79**, 5471 (1957).

(10) R. C. Cookson, M. J. Nye, and G. Subrahmanian, *J. Chem. Soc. C*, 473 (1967).

(11) The 2,4-diphenyl ketone **7** rather than the unsubstituted bicyclo-[3.2.1]oct-6-en-3-one was used in the present study, since it was anticipated that conversion of the latter to its dianion may be difficult at best.

(12) C. Mao, C. R. Hauser, and M. L. Miles, *J. Amer. Chem. Soc.*, **89**, 5303 (1967).

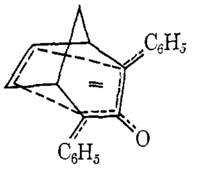
tetramethylsilane as an external reference and is displayed in Figure 1. The doublet (J = 4.0 Hz) centered at δ 3.64, and partly overlapped by the residual α-proton signal of the THF, was attributed to protons H_1 and H_5, and it presumably arises from coupling of $H_{1,5}$ with H_8'. The coupling of protons $H_{1,5}$ with H_8'' is near zero.[7b] The coupling constant between H_1,H_5 and H_6,H_7 was small, as was shown by spin decoupling experiments, discussed below.

The singlet at δ 5.41 integrated for two protons and was assigned to the vinylic hydrogens H_6 and H_7. Irradiation at the $H_{1,5}$ frequency sharpened the singlet at δ 5.41, and irradiation at the $H_{6,7}$ frequency resulted in considerable sharpening of the $H_{1,5}$ doublet.

The aromatic protons of the phenyl groups at $C_{2,4}$ appeared as three well-separated groups of signals, at δ 6.19 (triplet), 7.09 (triplet), and 7.59 (doublet), corresponding to the para, meta, and ortho protons, respectively.

The nmr signals corresponding to protons H_8' and H_8'' were presumably under the hexane absorptions[13] and could not be observed.

The most important information obtained from the nmr spectrum of dianion **9** is the large (1.05 ppm) upfield shift of the vinylic protons $H_{6,7}$, relative to the starting ketone **7** (see Experimental Section). This upfield shift, which is 87% as large as that experienced by the para protons of the aromatic rings at $C_{2,4}$, clearly indicates that the negative charge in the 2,4-diphenylbicyclooctenone dianion **9** has interacted not only with the carbonyl and phenyl groups, but also with the $C_{6,7}$ carbon–carbon double bond, and that it is best represented by structure **10**, which graphically demonstrates the participation of the β-olefinic group in the dispersal of the negative charge, and stresses its homoaromatic nature.



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In direct contrast to the large upfield shift experienced by the vinylic protons $H_{6,7}$, the bridgehead protons $H_{1,5}$ of dianion **9** actually moved downfield by 0.43 ppm, relative to $H_{1,5}$ in the starting ketone **7**. In line with the proposed homoaromatic nature of dianion **9**, the downfield shift of protons $H_{1,5}$ can be ascribed to the deshielding ring current effect of the homoaromatic cyclopentenone system which apparently offsets the shielding which protons $H_{1,5}$ are expected to experience due to field effects.[7b,14]

Quenching the dianion solutions with excess deuterium oxide gave 2,4-dideuterated ketone **7**-d_2, in 74% yield, as the only isolable product. As expected the nmr spectrum of the recovered ketone **7**-d_2 was devoid of absorption for α hydrogens.

The fact that deuteration of dianion **9** occurred exclusively at the C_2 and C_4 positions, despite delocalization of the negative charge at positions C_6 and C_7, is in line with previous reports concerning protonation and/or deuteration of homoaromatic carbanions,[7a,14] and is considered to be due to the fact that positions $C_{2,4}$ are kinetically much more favored than positions $C_{6,7}$.

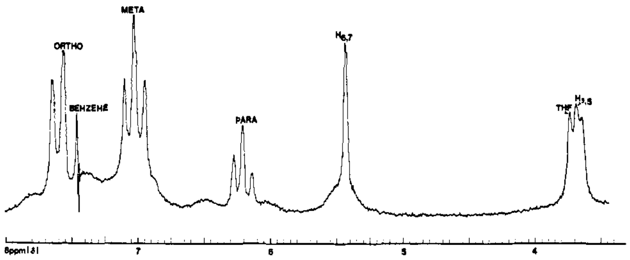
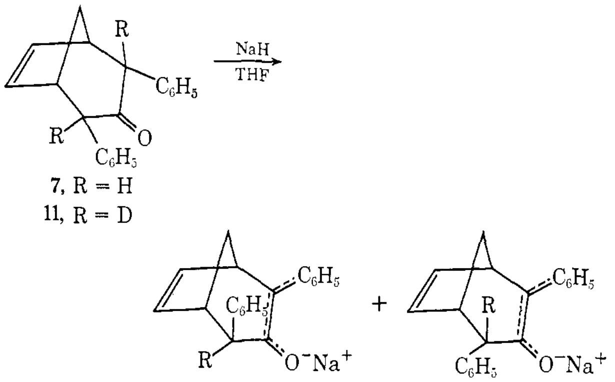


Figure 1. Nmr spectrum of 2,4-diphenylbicyclooctenone dianion **9** in THF-d_8–hexane recorded on a Varian XL-100 spectrometer using tetramethylsilane as an external reference.

Preparation and Properties of 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one Monanions 8a,b. In order to obtain direct information concerning possible long-range interactions in bicyclic enolate monoanions, bicyclic ketone **7** was converted to its monoanions **8a,b**, and their nmr spectrum was examined.

Isomeric enolates **8a,b** were easily formed by treatment of ketone **7** with sodium hydride in THF or THF-d_8, under equilibrating conditions. Thus, when ketone **7** was rapidly added to excess sodium hydride in THF at room temperature, 1 equiv of hydrogen gas was evolved, indicating complete monoionization. Subsequent quenching of the enolate solution with water afforded the starting ketone **7** in 91% yield, as shown by ir and nmr analysis of the crude reaction mixture.



7, R = H
11, R = D

8a
12a

8b
12b

The nmr spectrum of the mixture of isomeric enolates **8a** and **8b** in THF-d_8 was recorded on a Varian HA-100 instrument using tetramethylsilane as an external reference and is displayed in Figure 2. The signal for the endo proton H_{4a} of isomer **8a** appears as a sharp singlet at δ 3.18, while the signal for the exo proton H_{4b} of isomer **8b** appears as a doublet (J = 5 Hz) at δ 3.75, due to coupling with H_{5b}. Drieding stereomodels indicate that the H_{5a}–H_{4a} dihedral angle is near 80°, while the H_{5b}–H_{4b} dihedral angle is approximately 40°, thus accounting for the lack of spin coupling between H_{4a} and H_{5a}, as compared to the large coupling between H_{4b} and H_{5b}. That the signals at δ 3.18 and 3.75 were indeed due to protons H_{4a} and H_{4b}, respectively, was firmly established, by comparing the nmr spectrum of anions

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[13] Under the conditions used to record the nmr spectrum of dianion **9**, the hexane absorptions completely covered the area of the spectrum between δ 0.5 and 2.4.

[14] J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6562 (1968).

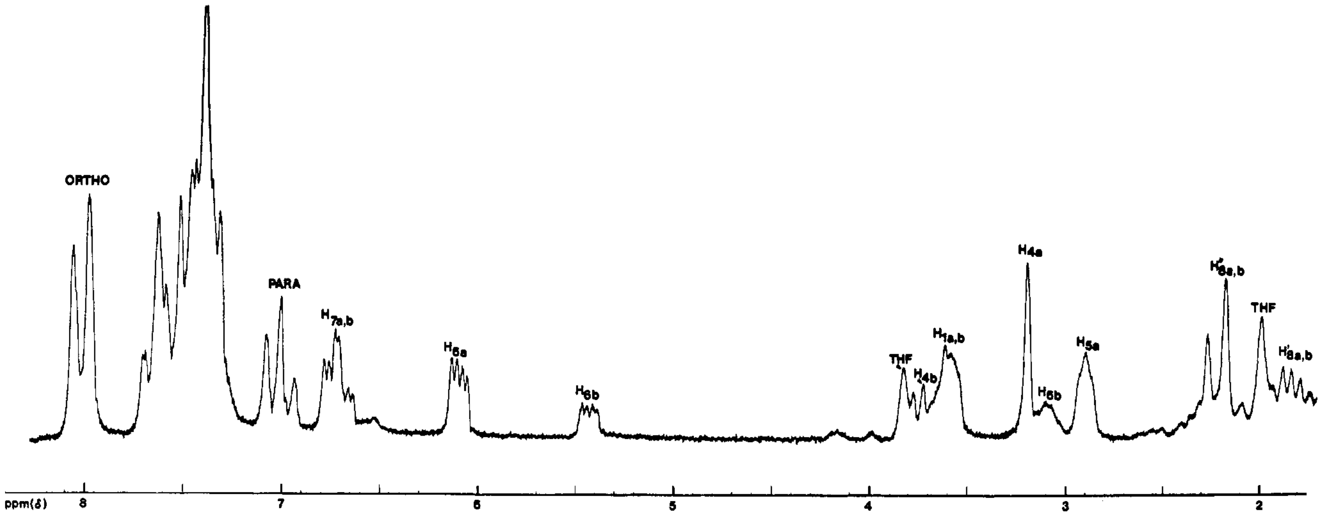


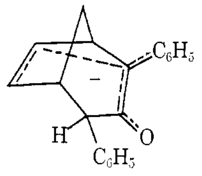
Figure 2. Nmr spectrum of 2,4-diphenylbicyclooctenone enolate monoanions **8a,b** in THF-d_8 recorded on a Varian HA-100 spectrometer using tetramethylsilane as an external reference.

8a,b (Figure 2) with that of enolate anions **12a,b**, which were formed by enolization of 2,4-dideuterated ketone **11**. The latter spectrum showed only residual signals at δ 3.18 and 3.75.

Proton H_{5a} appears as a triplet (J = 1.8 Hz) at δ 2.88, due to coupling with H_{6a} and H'_{8a}. Irradiation at H_{6a} reduced the triplet to a doublet. No coupling is observed between protons H_{5a} and H''_{8a}, since their dihedral angle is about 85°. Proton H_{5b} is coupled to H_{4b}, H_{6b}, and H_{8b} and appears as a broad multiplet[15] at δ 3.06. Protons $H_{1a,b}$ appear as a poorly resolved multiplet centered at δ 3.57. The vinylic protons H_{7a} and H_{7b} occurred each as a pair of doublets (partially overlapping) at δ 6.74 and 6.66, respectively, due to coupling with the protons at C_1 ($J_{1a,7a} = J_{1b,7b}$ = 3 Hz) and C_6 ($J_{6a,7a} = J_{6b,7b}$ = 6 Hz). Irradiation at H_{6a} simplified the left side of the pattern at δ 6.60–6.80, while irradiation at H_{6b} simplified the right side of the above pattern. In addition, simultaneous irradiation at $H_{1a,b}$ reduced the multiplet due to $H_{7a,b}$ to two doublets (J = 6 Hz) with their inner peaks overlapping, thus appearing as a triplet. Vinylic protons H_{6a} and H_{6b} resonate at δ 6.08 and 5.41, respectively, as pairs of doublets arising from coupling with H_{7a} and H_{7b} ($J_{6a,7a} = J_{6b,7b}$ = 6 Hz) and H_{5a} and H_{5b} ($J_{5a,6a} = J_{5b,6b}$ = 3 Hz). Irradiation at H_{5a} reduced the four-line pattern at δ 6.08 to just a doublet with the wide coupling (J = 6 Hz) retained, while irradiation at H_{7a} reduced the above pattern to a doublet with the narrow coupling (J = 3 Hz) retained. Similar decoupling experiments were satisfactorily performed with H_{5b} and H_{7b}. The signal for protons $H'_{8a,b}$ appears as a multiplet at δ 1.85, while that for $H''_{8a,b}$ appears as a doublet at δ 2.22.

Finally, the aromatic protons appear as a triplet at δ 7.00, assigned to the para proton of the phenyl ring at C_2, a multiplet centered at δ 7.60 attributed to the meta protons of the benzene ring at C_2 and all of the protons of the aromatic ring at C_4, and a doublet at δ 8.01, due to the ortho protons of the phenyl group at C_2.

The possibility of long-range interactions in isomeric enolates **8a,b** was next examined. Charge delocalization across the $C_{6,7}$ carbon–carbon double bond to give a homoallylic enolate as shown by structure **13** would



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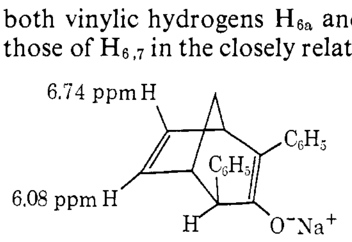
be expected to increase the electron density around C_6, thereby causing protons $H_{6a,b}$ to undergo an upfield chemical shift in the nmr. Examination of the nmr spectrum of isomeric enolates **8a,b** showed that protons H_{6a} and H_{6b} had undergone an upfield shift of 0.39 and 1.06 ppm, respectively, relative to the starting ketone **7**. The small upfield shift of proton H_{6a} of isomer **8a** can be rationalized on the basis of anisotropic effects due to the enolate carbon–carbon double bond at $C_{2,3}$ (structure **14**), and it is unlikely that homoconjugation occurred in this isomer. Indeed, the chemical shifts of both vinylic hydrogens H_{6a} and H_{7a} are quite similar to those of $H_{6,7}$ in the closely related system[7b] **15**.



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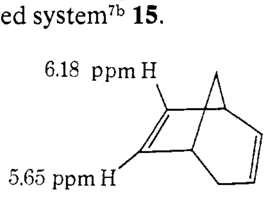

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On the other hand, the upfield shift of proton H_{6b} relative to the starting ketone **7** is considerably larger than that of H_{6a} and homoconjugation may be thought to have occurred in this case. However, it should be pointed out that in isomeric enolate **8b** the phenyl group at C_4 is in the endo position, and the larger upfield shift of proton H_{6b} relative to H_{6a} may well be due to the shielding ring current effect of the C_4 benzene ring.[16]

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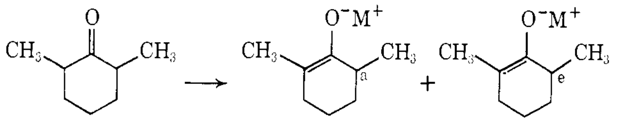
(15) The signal for proton H_{5b} is much better resolved in the spectrum of anions **12a,b**, where it appears at δ 3.06 as a triplet due to coupling with H_{6b} and H_{8b}. As expected, irradiation at H_{6b} reduced the triplet to a doublet.

(16) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N. Y., 1969, pp 72–102.

The above experimental results thus indicate that little or no homoallylic conjugation occurred in either of the isomeric enolate monoanions **8a** and **8b**. The lack of charge delocalization across the $C_{6,7}$ carbon–carbon double bond may be explained by taking into account the fact that the negative charge at C_2 can be stabilized through classical conjugation not only with the carbonyl group but also with one of the phenyl rings. Classical stabilization has been previously shown to greatly reduce and sometimes completely eliminate the tendency of a carbonium ion center to engage in nonclassical interactions,[17] and a similar effect in the case of carbanions is not surprising.

Next, the nature of the configurational composition of the mixture of the two isomeric enolates **8a** and **8b** was considered. Examination of the nmr spectrum of the mixture of anions **8a,b** (Figure 2) clearly shows that the absorptions due to protons H_{6a} and H_{6b} are well separated and could be conveniently used to estimate the amount of each isomer in the mixture. Integration of these absorptions showed that the two isomers were not produced in equal amounts, but instead, isomer **8a** predominated over **8b** by a ratio of 2:1. Since enolization of bicyclooctenone **7** was effected under equilibrating conditions, the amount of each isomer in the mixture should be a reflection of the thermodynamic stability of the two isomeric anions, and the conclusion can be drawn that isomer **8a** is more stable than isomer **8b**. Three points of particular interest then arise. First, why is isomer **8a** more stable than **8b**? Secondly, is the isomer distribution solvent dependent, and thirdly, since the parent ketone **7** may be regarded as a 2,6-disubstituted cyclohexanone with a vinyl bridge joining carbons C_3 and C_5, it would be pertinent to compare and contrast the behavior of the present system with that of simple 2,6-disubstituted cyclohexanones.

In connection with the last two points, Johnson[18] and his coworkers found that enolization of 2,6-dimethylcyclohexanone (**16**) afforded a mixture of isomeric enolates **17a** and **17b**, the exact ratio depending critically on the solvent used. The bulkier the solvent the more of isomer **17a** was produced. These results were explained[18] on the basis of the observation that the dihedral angle CH_3–C_6 and O^-M^+–C_1 is larger when the methyl group at C_6 is in the axial than when it is in the equatorial position. It was, then, theorized[17] that as the solvent became bulkier, the interaction between the solvated ion pair and the methyl group at C_6 became greater which in turn produced larger amounts of isomeric enolate **17a** at equilibrium.



16 **17a** **17b**

With these observations in mind, we proceeded to investigate whether the ratio of the isomeric enolates **8a** and **8b** produced from 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (**7**) was solvent dependent. For this purpose bicyclic ketone **7** was enolized with sodium hydride in dimethyl sulfoxide (DMSO) and hexamethylphosphoramide (HMPA) under conditions identical with those employed when THF was used as a solvent. Most interestingly, nmr examination of the reaction mixtures revealed that, unlike 2,6-dimethylcyclohexanone (**16**), the ratio of the two isomeric enolates from bicyclic ketone **7** was identical in all three solvents.

The marked difference in behavior between 2,6-dimethylcyclohexanone (**16**) and bicyclooctenone **7** is undoubtedly a direct result of the effect of the vinyl bridge on the stereochemistry of the cyclohexanone ring. Thus dreiding stereomodels clearly indicate that in the bicyclic enolates **8a,b** the dihedral angles between the oxygen of the carbonyl group and either the exo (axial) or endo (equatorial) bonds at C_4 are practically equal, thereby making the interaction of the solvated ion pair O^-Na^+ with the phenyl group to be the same regardless of whether the latter is in the exo or endo position.

Had the interaction between the phenyl group at C_4 and the solvated ion pair O^-Na^+ been the only factor controlling the configurational composition of the isomeric enolates derived from ketone 7, a 1:1 mixture of the two isomers would be expected to result. As mentioned earlier, however, isomer **8a**, with the C_4 phenyl in the exo (axial) position, predominated by a ratio of 2:1. This isomer distribution is believed to be a reflection of steric interactions between the ortho hydrogens of the C_4 phenyl ring and the hydrogens at C_6 and C_8. Indeed, Dreiding stereomodels clearly show that there is more steric interference between the ortho hydrogens of an endo phenyl ring and H_6 than there is between the ortho hydrogens of an exo phenyl ring and H_8''.

Experimental Section

General. Melting points were taken on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Vapor phase chromatographic (vpc) analyses were performed on a Varian Aerograph, Series 2700, gas chromatograph equipped with a thermal conductivity detector, and using helium as a carrier gas. A 5 ft × 0.25 in. column packed with 3% SE-30 on Varaport 30 was used. Infrared spectra (ir) were taken on a Beckman IR-8 infrared spectrophotometer, using the KBr pellet method. Nuclear magnetic resonance (nmr) spectra were obtained on a Varian Associates Model A-60, HA-100, and/or XL-100 spectrometer. All chemical shifts are reported in parts per million and all coupling constants are in hertz (Hz). An IEC International, Size 2, Model K, centrifuge was used.

All reactions involving carbanions were carried out in appropriate size three-necked, round-bottom flasks, under an atmosphere of high purity nitrogen.

Materials. 1,3-Diphenyl-2-propanone was purchased from Eastman Kodak Co., Rochester, N. Y. The sodium hydride was in a 57% mineral oil dispersion and was obtained from Alfa Inorganics, Beverly, Mass. Cyclopentadiene was obtained by distillation of 3α,4,7,7α-tetrahydro-4,7-methanoindene purchased from Matheson Coleman and Bell, East Rutherford, N. J. *n*-Butyllithium was a 1.58 *M* solution in hexane and was procured from Foote Mineral Co., Exton, Pa. Perdeuterated tetrahydrofuran (THF-d_8) was obtained from Columbia Organic Chemicals Co., Columbia, S. C.

2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (7). This compound was prepared essentially by the method of Cookson,[10] *et al.* For purposes of comparison, its nmr spectrum was recorded in THF, with an external TMS standard, and displayed the following resonances: δ 7.40 (m, 10 H, aromatic), 6.46 (t, 2 H, vinylic hydrogens at $C_{6,7}$), 4.1 (d, 2 H, $C_{2,4}$ hydrogens), 3.19 (m, 2 H, $C_{1,5}$ hydrogens), 2.48 (m, 2 H, C_8 hydrogens).

For details concerning the nmr spectrum of ketone 7 in $CDCl_3$, see ref 10.

Preparation of 2,4-Dideuterio-2,4-diphenylbicyclo[3.2.1]oct-6-en-

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[17] (a) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Amer. Chem. Soc.*, 74, 1113 (1952); (b) P. G. Gasman, J. Zeller, and J. T. Lumb, *Chem. Commun.*, 69 (1968).

[18] (a) S. K. Malhotra and F. Johnson, *J. Amer. Chem. Soc.*, 87, 5513 (1965); (b) F. Johnson, *Chem. Rev.*, 68, 375 (1968).

3-one (7-d_2). 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (7) (1.5 g, 0.0055 mol) and sodium hydride (0.01 g, 0.0006 mol) in 100 ml of dioxane and 20 ml of deuterium oxide was stirred for 72 hr at room temperature. The reaction mixture was then extracted with chloroform and dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. There was obtained 1.2 g of dideuterated ketone 7-d_2: nmr (CDCl$_3$) δ 7.23 (m, 10 H, aromatic), 6.23 (t, 2 H, vinylic hydrogens H$_{6,7}$), 2.98 (m, 2 H, bridgehead hydrogens H$_{1,5}$) and 2.18 (m, 2 H, hydrogens H$_8'$, H$_8''$).

Formation of 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one Monoanions 8a,b and 12a,b. (a) Formation of Monoanions 8a,b in THF. This reaction, as well as each of the subsequently described monoanion formations, was carried out in a 15-ml, three-necked, round-bottom flask equipped with a magnetic stirrer, a septum, and a condenser connected to a gas collection apparatus consisting of an inverted 250-ml graduated cylinder filled with water. The flask was charged with 0.09 g (0.0037 mol) of sodium hydride, flushed with nitrogen, and closed to the atmosphere. A solution of 0.5 g (0.0018 mol) of 2,4-diphenylbicyclo[3.2.1]oct-6-en-3-one (7) in 3 ml of THF was introduced into the reaction flask through the septum by means of a syringe. Reaction occurred quite readily as shown by the immediate evolution of hydrogen and was completed within 1 hr. The reaction mixture was then quenched with 4 ml of water. The organic layer was dried over magnesium sulfate and evaporated under reduced pressure to give 0.455 g (91% yield) of the starting ketone 7, as shown by ir and nmr analysis of the crude reaction product.

In another experiment, a solution of 0.5 g (0.0018 mol) of ketone 7 in 2 ml of THF-d_8 was added to 0.09 g (0.0037 mol) of sodium hydride and the reaction mixture was stirred until 1 equiv of hydrogen gas had been evolved. Stirring was then discontinued, the excess sodium hydride was allowed to settle to the bottom of the flask, the supernatant brown liquid was transferred by means of a syringe into an nmr tube equipped with a septum, and the nmr tube was flushed with nitrogen. The nmr tube was centrifuged for 3–4 min at 1500 rpm, the liquid was transferred into a second nmr tube, and the spectrum of the solution was recorded on a Varian A-60 and an HA-100 instrument. The 100-MHz spectrum of the solution is shown in Figure 2. Integration of the peaks corresponding to protons H$_{6a}$ and H$_{6b}$ in the 60-MHz spectrum showed that isomeric enolates 8a and 8b were present in a ratio of 2:1.

(b) Formation of Monoanions 8a,b in DMSO and HMPA. 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (7) (0.5 g, 0.0018 mol) in 2 ml of DMSO or HMPA was treated with 0.09 g (0.0037 mol) of sodium hydride as described above, and the nmr spectrum of the resulting monoanions was recorded on a Varian A-60 instrument. The resonances observed were the same as those found for monoanions 8a,b in THF-d_8, except that the signals below δ 4.5 were obscured by the solvents. The ratio of the peaks corresponding to protons H$_{6a}$ and H$_{6b}$ was 2:1. Subsequent quenching of the solutions with water produced the starting ketone 7.

(c) Formation of Monoanions 12a,b in THF. 2,4-Dideuterated ketone 7-d_2 (0.5 g, 0.0018 mol) was treated with 0.09 g (0.0037 mol) of sodium hydride as described above and was subsequently quenched with deuterium oxide to give 0.40 g (80% yield) of starting ketone 7-d_2, as shown by ir and nmr analysis of the crude reaction mixture.

In another experiment, monoanions 12a,b were formed from 0.5 g (0.0018 mol) of ketone 7-d_2 and 0.09 g (0.0037 mol) of sodium hydride in 2 ml of THF-d_8, and the spectrum of the solution was recorded on a Varian HA-100 instrument. The spectrum was practically identical with that of enolates 8a,b (Figure 2), except that the former had only residual peaks at δ 3.18 and 3.75.

Formation of 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one Dianion 9 in THF and Subsequent Deuteration with Deuterium Oxide. 2,4-Diphenylbicyclo[3.2.1]oct-6-en-3-one (7) (0.5 g, 0.0018 mol) was treated with 0.09 g (0.0037 mol) of sodium hydride in 2 ml of THF as described earlier to produce the monoanions 8a,b. The reaction was then treated with 2 ml (0.00316 mol) of 1.58 *M* solution of *n*-butyllithium in hexane and was stirred for 4 hr. The brick-red solution was then cooled to −5° and quenched with 4 ml of deuteium oxide, to give 0.37 g (74%) of dideuterated ketone 7-d_2, as shown by gas chromatographic analysis and nmr of the crude reaction mixture.

In another experiment dianion 9 was formed in THF-d_8 as described above and the brick-red solution was then transferred into an nmr tube containing a sealed capillary tube with TMS, and the nmr spectrum was recorded on a Varian XL-100 instrument. The spectrum is displayed in Figure 1.

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Reactions of 1,1-Dimethyldiazenium Bromide with Bicyclic Olefins. *N*-(Dimethylamino)aziridines

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Abstract: Norbornadiene (3) reacts with 1,1-dimethyldiazenium bromide (1) in 1.5 *M* hydrobromic acid to give 52% of the *endo-N*-dimethylaminoaziridine (6), 4% of the other endo product 7, and 39% of **8**, **9**, **10**, and **11**, nortricyclene products of exo attack. The relative yields of **7**–**11** are greater with increasing hydrobromic acid concentrations, and that of **6** diminishes. Endo addition to such an extent is attributed to preliminary 2,6 cycloaddition of **1** to **3**, and it has been shown to be reversible. Norbornene **2** also gives the aziridine **4** (here the exo isomer) and **5**. The reaction of **4** with hydrobromic acid has been shown to give **5**. *endo*-5-Norbornene-2-methanol gives **13**, and benzonorbornadiene gives **14**, products expected from their prior electrophilic additions.

In hydrobromic acid 1,1-dimethyldiazenium bromide (1) adds like a dienophile to 1,3-alkadienes[1] and like an electrophile with some styrenes,[1b] but it does not react with ordinary olefins. However, such reactions occur with the more reactive bicyclic olefins. With norbornene (2) or norbornadiene (3), the exo or endoaziridines (4 or 6) are important products. Both are remarkably stable in the aqueous acidic reaction mixtures. *endo*-5-Norbornene-2-methanol and benzonorbornadiene give expected products.[2,3]

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