which, after recrystallization from 95% alcohol, afforded a white, crystalline solid, mp 153–155°. This material was assigned as the Diels–Alder adduct **18** on the basis of the following data. The infrared spectrum was characterized by bands at 3.50, 6.95, 7.45, 7.68, 9.85, 10.20, 13.31, and 14.40 μ. The mass spectrum showed a parent peak at *m/e* 378 and had peaks at 360 and 270 (base). The nmr spectrum (CCl_4) had multiplets at τ 2.3–3.20, 6.91–7.21, and 7.61–8.90.

Anal. Calcd for $C_{28}H_{26}O$: C, 88.85; H, 6.92. Found: C, 88.62; H, 6.92.

Dimerization of *cis,trans*-1,3-Cyclooctadiene in the Presence of Maleic Anhydride. A solution of 0.08 g of *cis,trans*-1,3-cyclooctadiene and 0.2 g of maleic anhydride in 5 ml of toluene was heated at reflux for 1 hr. During this time a white solid precipitated from the reaction mixture. Vapor-phase chromatographic analysis of the solution showed the dimers present in the normal ratio. Evaporation of the solvent left a white solid, mp 305–325°. The infrared spectrum (KBr) of this material showed bands at 3.5, 5.4, 5.6, 6.7, 8.2, 9.2, and 10.9 μ. The material was insoluble in all solvents and resisted sublimation and therefore was not characterized further.

Kinetic Runs. A measured amount of *cis,trans*-1,3-cyclooctadiene and diethyl phthalate (internal standard) was placed in a 10-ml Pyrex test tube that had been thoroughly cleansed and dried in an oven. The mixture was diluted with pure cyclohexane to give 1.0 *M* solutions. A Neslab Instruments constant temperature apparatus, accurate to ±0.01°, was used for the high-temperature runs. A Wilkens-Anderson Lo-Temp refrigeration unit was used to control the bath at the lower temperatures. Thermolysis mixtures were analyzed by vpc. At the end of each time interval the tubes were quenched prior to gas-chromatographic analysis. The reciprocal of the difference between original concentration of diene and amount of dimers produced was plotted against time to give the rate. The results are summarized in Table III.

Acknowledgment. One of us (A. P.) acknowledges the support of this work by the National Science Foundation (Grant GP-24449).

Electron and Energy Transfer between Bicyclo[2.2.2]octane Bridgehead Moieties

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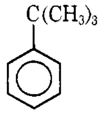
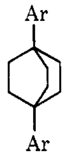
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received September 1, 1970*

Abstract: 1,4-Diphenylbicyclo[2.2.2]octane, 1,4-bis(*p*-cyanophenyl)bicyclo[2.2.2]octane, 1,4-bis(*p*-nitrophenyl)-bicyclo[2.2.2]octane, and 1-benzoyl-4-(α-naphthyl)bicyclo[2.2.2]octane were synthesized for energy and electron-transfer studies. Introduction of an odd electron into one aromatic ring of the symmetrical diaryl derivatives led to radical anions in which the odd electron was localized in one of the two rings. This result is analyzed as a tunneling problem consisting of a single potential energy barrier corresponding to the bicyclic ring structure. In contrast, the study of energy transfer in the naphthyl–benzoyl derivative provided evidence for singlet transfer from naphthyl to benzoyl and triplet transfer from benzoyl to naphthyl. The singlet transfer is considered to involve a dipole–dipole mechanism. The triplet–triplet transfer provides evidence that close approach is not invariably required.

Related to our studies on the problem of electron transfer between orthogonal π systems[1] was the question of the facility of transfer of electrons and electronic excitation through saturated hydrocarbon insulators. For this study, 1,4-disubstituted bicyclo[2.2.2]octane derivatives were selected, since the bicyclo[2.2.2]octane moiety provides a symmetrical and convenient framework assuring lack of approach of orbitals of the separate π systems.[2]

Also, it is observed experimentally[3,4] that line broadening occurs in the esr spectra of *tert*-butyl aromatic radical anions due to appearance of odd electron density in the β carbon–hydrogen bonds. If there is similar penetration to β carbon–carbon bonds in a 1,4-disubstituted bicyclo[2.2.2]octane derivative as **1**, then this would suggest the ability to delocalize odd electron density to the second ring, since three carbon–carbon bonds are β to both rings.[5]





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Similarly, extended Hückel calculations (*vide infra*) show weighting of the bicyclooctane σ orbitals in the first antibonding MO along with both of the aromatic rings. Hence, there seemed to be the *a priori* possibility of both electron and energy delocalization between rings.

Synthetic Aspects. A synthesis[6] which promised to be of general use began with cyanoethylation of an aryl acetone (**2**), aryl being phenyl or naphthyl as shown in Chart I. Hydrolysis, cyclization, and internal acid-catalyzed aldolization led to **6**. Wolff–Kishner reduction, conversion to the bridgehead chloride (**8**), and Friedel–Crafts reaction with benzene afforded 1,4-diphenylbicyclo[2.2.2]octane (**9**).[7] Nitra-

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[1] H. E. Zimmerman and J. R. Dodd, *J. Amer. Chem. Soc.*, **92**, 6507 (1970).

[2] Recent examples of excitation transfer in rigid systems include: (a) R. A. Keller and L. J. Dolby, *ibid.*, **91**, 1293 (1969); (b) S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid*, **87**, 995 (1965); (c) A. A. Lamola, *ibid.*, **91**, 4786 (1969).

[3] J. R. Bolton, A. Carrington, A. Forman, and L. E. Orgel, *Mol. Phys.*, **5**, 43 (1962).

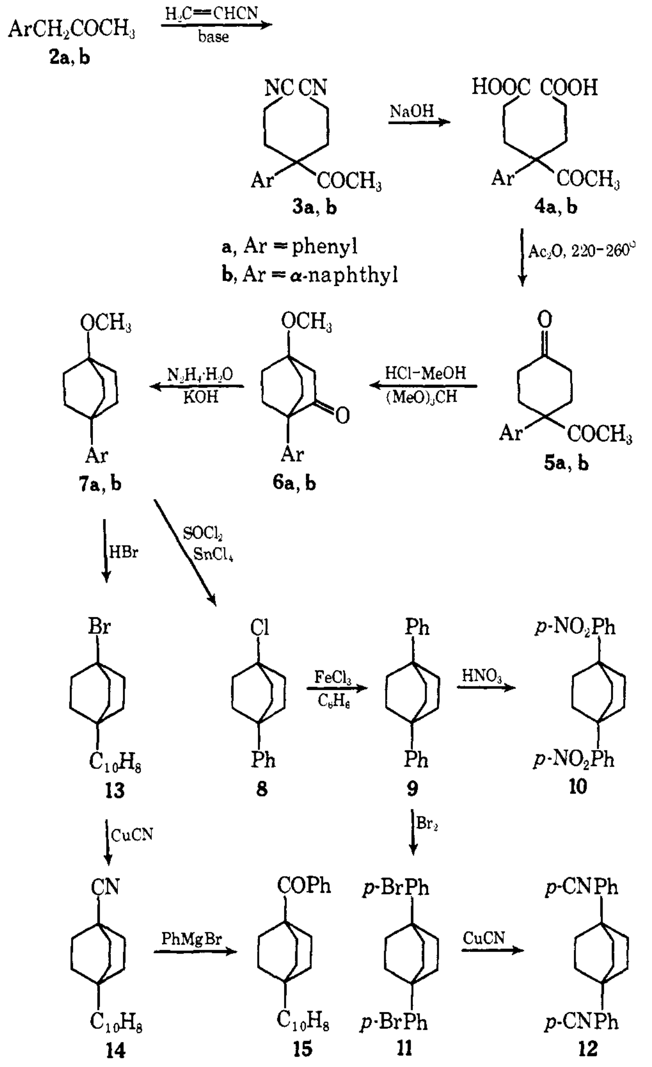
[4] P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963).

[5] Similar studies on the *p*-cyclophanes have been done: F. Gerson and W. B. Martin, Jr., *J. Amer. Chem. Soc.*, **91**, 1883 (1969); S. I. Weissman, *ibid.*, **80**, 6462 (1958).

[6] The initial steps of the synthesis were patterned after the preparation of 4-methoxy-1-phenylbicyclo[2.2.2]octan-2-one and 1-chloro-4-methylbicyclo[2.2.2]octane as described by K. Morita and T. Kobayashi, *J. Org. Chem.*, **31**, 229 (1966); Z. Suzuki and K. Morita, *ibid.*, **32**, 31 (1967).

[7] After completion of this research, a similar synthesis of 1,4-diphenylbicyclo[2.2.2]octane was published by N. B. Chapman, S. Sotheeswaran, and K. J. Toyne, *ibid.*, **35**, 917 (1970).

Chart I. Synthesis of 1,4-Disubstituted Bicyclo[2.2.2]octanes



tion gave 1,4-bis(*p*-nitrophenyl)bicyclo[2.2.2]octane (**10**), while bromination followed by reaction with cuprous cyanide gave 1,4-bis(*p*-cyanophenyl)bicyclo-[2.2.2]octane (**12**). Conversion of **7b** to the bridgehead bromide **13** and reaction with cuprous cyanide followed by treatment with phenylmagnesium bromide gave 1-benzoyl-4-(α-naphthyl)bicyclo[2.2.2]octane (**15**).

Results

Electron Introduction. For electron-transmission studies, an approach involving esr spectroscopy of monoradical anions was used in order to determine whether the electron introduced was localized in one ring or, alternatively, delocalized over both. For electron introduction, sodium–potassium alloy in ethereal solvents was used. Also potassium *tert*-butoxide in DMSO was used for the nitro compound. The results of the esr spectra are summarized in Table I along with those of appropriate model compounds.

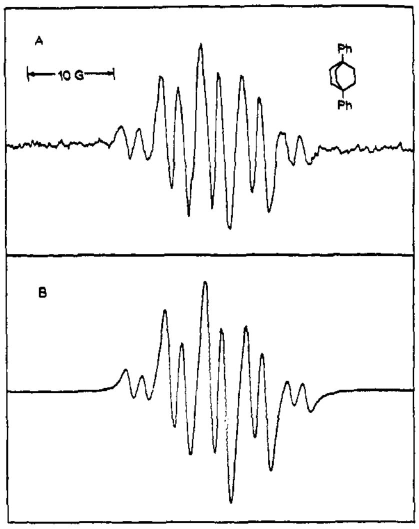


Figure 1. Esr spectrum of 1,4-diphenylbicyclo[2.2.2]octane: A, experimental; B, computer simulation.

Table I. Esr Hyperfine Coupling Constants

Compound (condn)	a_0, G	a_m, G	a_p, G	a_N, G	Line width, G
Diphenyl[a] (THF–DME, 2:1, −90°)[b]	4.66	4.66	1.78		0.9
tert-Butylbenzene (DME, −70°)[c]	4.66	4.66	1.74		0.9
Dinitro[d] (THF–DME, 2:1, 25°)[b]	1.12	3.44		10.9	0.5
Dinitro[d] (DMSO, *tert*-BuOK, 25°)[b]	1.02	3.15		9.95	0.5
p-Nitro-*tert*-butylbenzene (EtOH)[e]	1.1	3.4		14.0	br.
Dicyano[f] (THF, −90°)[b]		4.12		2.25	1.3
Dicyano[f] (DME, −90°)[b]		3.80		2.55	1.3
Dicyano[f] (THF–DME, 2:1, −90°)[b]		4.00		2.00	1.0
p-Cyanotoluene (DME–THF, 3:1, −100°)[g]	0.64	4.13		2.07	0.3

[a] 1,4-Diphenylbicyclo[2.2.2]octane. [b] This work. [c] Reference 3. [d] 1,4-Bis(*p*-nitrophenyl)bicyclo[2.2.2]octane. [e] Reference 4. [f] 1,4-Bis(*p*-cyanophenyl)bicyclo[2.2.2]octane. [g] Reference 8.

Reduction of a degassed sample of 1,4-diphenylbicyclo[2.2.2]octane with sodium–potassium alloy at −90° gave a solution of the corresponding radical anion. The esr spectrum (Figure 1) consisted of five doublets with the approximate intensity ratios of 1:4:6:4:1. This corresponds to the electron coupling with four ring protons with equal hyperfine coupling constants and additional coupling with a fifth proton having a smaller coupling constant. This spectrum is in excellent agreement with that reported for *tert*-butylbenzene[3] and with computer simulation. An upper limit on the rate of electron transfer between rings can be determined,[9] based on the line width. This width is broadened additionally by unresolved β hydrogen coupling. Such calculation indicates that the rate of electron transfer between rings is less than 3×10^6 sec^{-1}.

Similarly, reduction of 1,4-bis(*p*-nitrophenyl)bicyclo[2.2.2]octane at room temperature in the same solvent gave an esr spectrum showing splitting from only the one nitrogen atom and two sets of two equivalent protons of a single aromatic ring. This is in good agreement with the spectrum reported for *p*-nitro-*tert*-butylbenzene. Here, the upper limit of the rate

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(8) A. Carrington and P. F. Todd, *Mol. Phys.*, **6**, 161 (1963).

(9) (a) This upper limit is obtained by multiplying the observed line width by 2.8×10^6 sec^{-1} (note ref 9b); (b) J. E. Harriman and A. H. Maki, *J. Chem. Phys.*, **39**, 778 (1963).

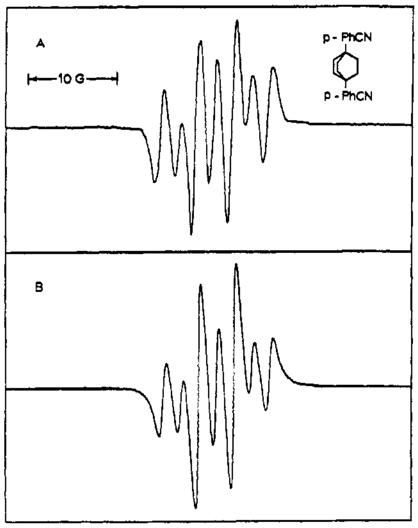

Figure 2. Esr spectrum of 1,4-bis(p-cyanophenyl)bicyclo[2.2.2]-octane: A, experimental; B, computer simulation.

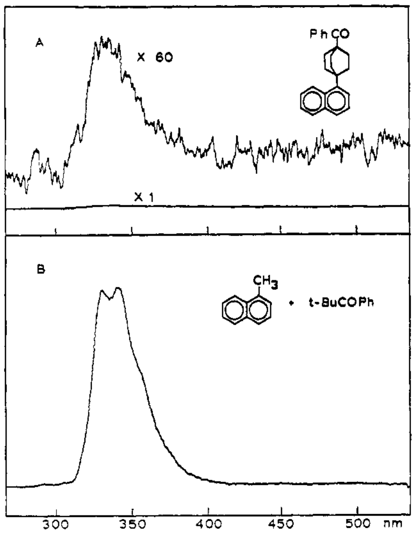

Figure 3. Fluorescence spectra of 1-benzoyl-4-(α-naphthyl)bicyclo[2.2.2]octane (A) and a mixture of 1-methylnaphthalene and pivalophenone (B). Excitation is at 295 nm. Concentrations are 0.0002 *M*.

of transfer is less than 1.5×10^6 sec^{-1}. A very similar spectrum was obtained using potassium *tert*-butoxide as reducing agent in dimethyl sulfoxide according to the method of Russell and Janzen.[10]

Reduction of 1,4-bis(p-cyanophenyl)bicyclo[2.2.2]octane with sodium–potassium alloy also gave an esr spectrum showing splitting from only one nitrogen atom (see Figure 2). Splitting is also observed for two equivalent ring protons. The spectrum has the same features in dimethoxyethane, tetrahydrofuran, and a 2:1 mixture of tetrahydrofuran–dimethoxyethane at −90°. The coupling constants varied slightly with solvent (note Table I). These coupling constants are in excellent agreement with those reported for p-cyanotoluene[8] and indicate that the odd electron is localized in one aromatic ring. Due to line broadening caused by the unresolved β hydrogen splitting, the splitting from the ortho hydrogens was not resolved. The line width indicates a rate of transfer of less than 3×10^6 sec^{-1}.

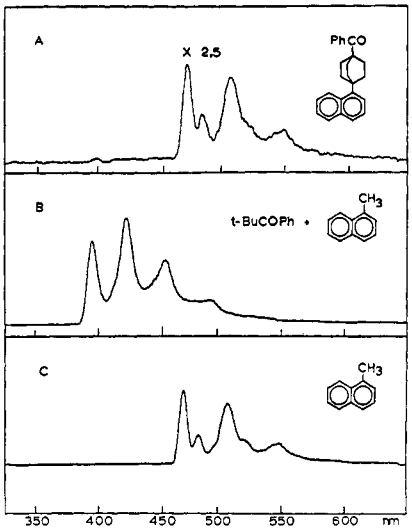

Figure 4. Phosphorescence spectra of 1-benzoyl-4-(α-naphthyl)-bicyclo[2.2.2]octane (A), a mixture of 1-methylnaphthalene and pivalophenone (B), and 1-methylnaphthalene (C). Excitation of A and B is at 350 nm, while C is at 295 nm. Concentrations are 0.001 *M*.

Thus, in all three cases, electron transfer between the two aromatic rings is not observed. These upper limits for the rates are almost certainly too high due to line broadening caused by unresolved coupling of the β hydrogens in the bicyclooctane system.

Electronic Excitation Transfer. For a study of the question of transmission of singlet and triplet electronic excitation through an aliphatic framework, the 1-benzoyl-4-(α-naphthyl)bicyclo[2.2.2]octane system was selected. This had the advantage that either chromophore could be selectively excited by proper choice of wavelength of incident light (*i.e.*, 295 *vs.* 350 nm) and that an exothermic transfer process was available to each chromophore *via* singlet or triplet excitation transfer.

Irradiation of 0.0002 *M* 1-benzoyl-4-(α-naphthyl)-bicyclo[2.2.2]octane (**15**) in cyclohexane at 295 nm, where the naphthyl group should receive 95% of the light absorbed, gave a fluorescence spectrum which was only 1% as intense as an equimolar solution of the model compounds, pivalophenone and 1-methylnaphthalene, at the same concentration (see Figure 3). This is most reasonably interpreted as deriving from essentially complete transfer of singlet excitation in **15** from the naphthyl group to the benzoyl moiety with resulting fluorescence quenching. Since at this concentration the model compounds did not show intermolecular transfer, as shown by comparison with the intensity of the fluorescence spectrum of 1-methylnaphthalene, the transfer in **15** is intramolecular.

Irradiation of 0.001 *M* 1-benzoyl-4-(α-naphthyl)bicyclo[2.2.2]octane (**15**) at 350 nm in 4:1 methylcyclohexane–isopentane glass at 77°K should give selective excitation of the benzoyl chromophore. The phosphorescence spectrum showed emission only from the naphthyl group (see Figure 4), even at a concentration of 0.0001 *M*. This is in contrast to an equimolar solution of pivalophenone and 1-methylnaphthalene, which showed emission only from the benzoyl group at concentrations as high as 0.01 *M*. Partial intermolecular

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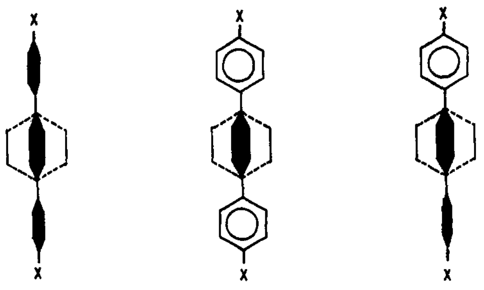
(10) G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, **84**, 4153 (1962).



16 17 18

Figure 5. Three conformations used in extended Hückel calculations. Conformations are the same in both **9** and **12**.

transfer in the model compounds could be seen at 0.1 *M*. Thus, complete triplet excitation transfer was taking place from the benzoyl chromophore to the naphthyl group in compound **15**. Such transfer must be intramolecular, since even partial intermolecular transfer did not occur in the model compounds until the concentration was 0.1 *M*.

Interpretative Discussion

Electron Transfer. The above esr results clearly indicate that in the radical anions of 1,4-diphenylbicyclo[2.2.2]octane (**9**), 1,4-bis(*p*-nitrophenyl)bicyclo-[2.2.2]octane (**10**), and 1,4-bis(*p*-cyanophenyl)bicyclo-[2.2.2]octane (**12**) the odd electron is confined to a single aromatic ring and is not delocalized between the two. That this localization was not due to ion pairing with the alkali metal gegenion is indicated by the observation of the same esr spectrum for 1,4-bis(*p*-cyanophenyl)bicyclo[2.2.2]octane in three different solvents, including dimethoxyethane, where ion pairing would be minimized.[11] Additionally, in the case of the radical anion of 1,4-bis(*p*-nitrophenyl)bicyclo[2.2.2]-octane, even the solvent dimethyl sulfoxide gave the localized anion, and one would not expect ion pairing in this highly polar solvent.

The observed electron localization is of interest when one considers the possibility for electron transfer through the bicyclooctane framework as suggested by extended Hückel calculations[12] on such systems.[13] Thus, in the antibonding MO's for compounds **9** and **12** a finite weighting of the bicyclooctane σ orbitals is found; note Table II where the sums of the squares of the coefficients for each portion of the molecules are given for the first antibonding and the three highest energy bonding molecular orbitals. This is true for several different conformations (note Figure 5).

Thus, the mere existence of finite electron density predicted for the first antibonding MO is seen to be insufficient for electron transmission in the radical anion. One aspect which one might consider is the importance of the weighting of the bicyclooctane basis orbitals in the first antibonding MO. As this weighting diminishes and approaches zero, one might expect an increased barrier to electron transmission.

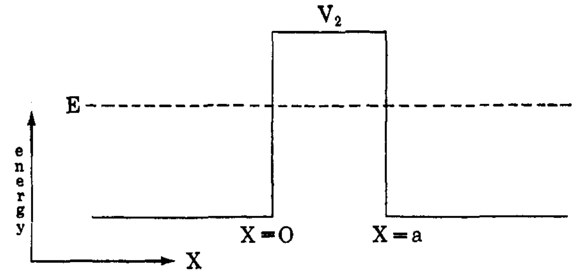


Figure 6. Barrier potential.

Table II. Weighting[a] of HBMO and LAMO Orbitals for Three Conformations

Species, MO (energy, eV)	Ring A	Bicyclo-octane	Ring B
1,4-Diphenylbicyclo[2.2.2]octane			
Conformation **16**			
LAMO (MO 52) (−8.2141)	0.6785	0.0044	0.6785
HBMO (MO 51) (−11.8206)	0.1140	0.5662	0.1140
MO 50 (−12.0016)	0.1896	0.4906	0.1896
MO 49 (−12.0425)	0.1405	0.5410	0.1405
Conformation **17**			
LAMO (MO 52) (−8.2046)	0.6802	0.0024	0.6802
HBMO (MO 51) (−11.7495)	0.1254	0.5394	0.1254
MO 50 (−12.0020)	0.1889	0.4928	0.1889
MO 49 (−12.0262)	0.1395	0.5219	0.1395
Conformation **18**			
LAMO (MO 53)[b] (−8.2005)	0.5148	0.0030	0.8452
LAMO (MO 52)[b] (−8.2091)	0.8473	0.0031	0.5114
HBMO (MO 51) (−11.8738)	0.0837	0.5336	0.0733
MO 50 (−11.9212)	0.1435	0.5225	0.1930
MO 49 (−12.0131)	0.1927	0.5019	0.1658
1,4-Bis(*p*-cyanophenyl)bicyclo[2.2.2]octane			
Conformation **16**			
LAMO (MO 60) (−9.1889)	0.6242	0.0194	0.6242
HBMO (MO 59) (−11.8274)	0.1114	0.5838	0.1114
MO 58 (−12.0114)	0.1847	0.5003	0.1847
MO 57 (−12.0879)	0.1149	0.5785	0.1149
Conformation **17**			
LAMO (MO 60) (−9.1875)	0.6242	0.0181	0.6242
HBMO (MO 59) (−11.7578)	0.1229	0.7912	0.1229
MO 58 (−12.0119)	0.1895	0.5241	0.1895
MO 57 (−12.0675)	0.1200	0.5566	0.1200
Conformation **18**			
LAMO (MO 61)[b] (−9.1804)	1.2486	0.0216	0.0002
LAMO (MO 60)[b] (−9.1806)	0.0001	0.0215	1.2484
HBMO (MO 59) (−11.8941)	0.0772	0.5456	0.1824
MO 58 (−11.9417)	0.1545	0.6309	0.1179
MO 57 (−12.0265)	0.2463	0.5187	0.2080

[a] Sums of the squares of the coefficients for all atoms (except hydrogen) in each portion of the molecules. [b] Essentially degenerate pair.

One approach which is helpful in assessing the situation is to consider an electron tunnelling through a potential barrier of varying height and thickness[14] (note Figure 6).[15] An electron in such a system will have a finite probability of penetrating the barrier. In the present situation one would analogize between height of the energy barrier and the energy difference of the first antibonding MO of an isolated bicyclooctane moiety relative to that of an isolated aromatic group.

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[11] (a) Ion pairing leading to perturbation of odd electron densities was observed by Gerson and Martin[5] in the paracyclophanes in tetrahydrofuran, but not in dimethoxyethane; (b) similar results were obtained by Zimmerman and Dodd[1] in the case of hexa-*tert*-butyltolan.

[12] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); F. P. Boer, M. D. Newton, and W. N. Lipscomb, *Proc. Nat. Acad. Sci. U. S.*, **52**, 890 (1964).

[13] We wish to thank Dr. Thomas W. Flechtner for carrying out these calculations.

[14] C. W. N. Cumper, "Wave Mechanics for Chemists," Academic Press, New York, N. Y., 1966, p 35; R. M. Eisberg, "Fundamentals of Modern Physics," Wiley, New York, N. Y., 1964, p 231.

[15] A double well model separated by a single barrier is not suitable since it gives standing wave solutions, rather than a probability of transfer.

The thickness of the barrier then represents the degree to which the bicyclooctane structure is a perfect insulator and therefore the weighting of this moiety in the first antibonding MO. The probability of electron transmission through the barrier is given in eq 1, where

$$T = 16\frac{E}{V_2}(1 - E/V_2)\exp\left[\frac{-4\pi a}{h}\sqrt{2m(V_2 - E)}\right] \quad (1)$$

E and m are the energy and the mass of the electron. This equation shows that the probability of transmission, T, depends on the thickness of the barrier, a, the height of the barrier, V_2, and the energy of the electron, E. The probability and rate of transmission in the barrier model should be related to the rate of electron transfer in the radical anions. Thus, the amount of weighting of the bicyclooctane moiety in the first antibonding MO should be important in determining the transmission rate.

Electronic Excitation Transfer. Discussion is needed of the observation that excitation of one end of the molecule resulted in transfer to the other end in both the singlet and triplet cases. As noted in the Results, with naphthyl light absorption the singlet excitation energy of this naphthyl end of the molecule is dissipated by the presence of the benzoyl group at the other end. It is then reasonable to assume, as noted above, that the mechanism of dissipation involves actual intramolecular energy transfer to the benzoyl moiety. Since at room temperature, singlet excitation of aromatic ketones does not lead to appreciable[16] fluorescence or phosphorescence, emission from benzoyl could not be used to check this conclusion.

For the singlet energy transfer responsible for quenching of naphthyl fluorescence, no dramatic rationale is needed. There is considerable literature on long-range dipole–dipole singlet excitation transfer, which is known to occur over distances up to 100 Å.[17] The transfer efficiency T is known to depend upon the relative orientation K of the transition dipole vectors as given in Förster's equation[17] as corrected by Latt[2b] (eq 2). In these equations, R_0 is the distance where transfer is 50% efficient, R is the distance between the chromophores, Q is the quantum yield for emission of the donor when isolated, J is the spectral overlap integral, n is the refractive index of the medium, N is Avogadro's number, ϕ_{AB} is the angle between the transition dipoles, and ϕ_A and ϕ_B are the angles between each of the dipoles and the line connecting the chromophores

$$T = (R_0/R)^6/[1 + (R_0/R)^6]$$

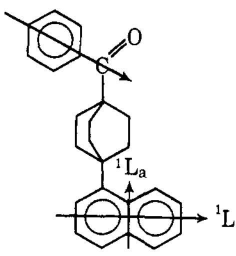
where

$$R_0^6 = \frac{9000J \ln 10K^2Q}{128\pi^5 n^4 N} \quad (2)$$

and

$$K = \cos\phi_{AB} - 3\cos\phi_A\cos\phi_B$$

Although this equation does not strictly apply for distances less than approximately 10 Å,[2c] it does lead to the conclusion that transfer should be very efficient for the conformation **19** in which the transition dipoles are as shown. Analysis is complicated by the fact that selective excitation of the naphthyl group required irradiation at 295 nm, and this wavelength leads to excitation of two naphthalene excited singlets due to spectral overlap between the ^1L_a band at 276 nm and the ^1L_b band at 313 nm. However these are short and long axis polarized,[18] respectively, and since neither of these transition dipoles is oriented perpendicular to the benzoyl transition dipole,[19] singlet dipole–dipole resonance transfer should be allowed. Such transfer is therefore in accord with the observed singlet excitation migration.



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Turning now to the observation of triplet excitation transfer, we note that for the present case, ordinary dipole–dipole transfer of the triplet excitation is unlikely. Thus, the Förster R_0 value for triplet excitation transfer from benzophenone to naphthalene with random orientation has been calculated[19b] to be 0.18 Å; the distance between chromophores in **19** is 7.0 Å and much larger. Similarly, a contact exchange mechanism is precluded by the bicyclooctane framework, which prevents collision of the two chromophores. However, the earlier discussion in connection with electron transfer may be extended to the problem of triplet excitation transfer.

Reference to Table II gives a clue to the observed facile triplet excitation delocalization. This table reveals that in contrast to the inappreciable weighting of the lowest energy antibonding MO in the bicyclooctane nucleus, the highest bonding MO is very heavily weighted in this moiety for the 1,4-diarylbicyclo[2.2.2]-octanes.[20] This means that a species lacking an electron in the highest bonding MO will have the "electron hole" delocalized throughout the molecule. Thus, in such molecules one would expect the electronic excited states to have the excitation delocalized to a considerable extent. The distribution of the positive electron hole through the entire molecule, including the bicyclooctane ring structure, should facilitate penetration of the antibonding electron by making the core of this bicyclic moiety more positive. This is equivalent to saying that the presence of the positive electron hole

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[16] Recent reports of room-temperature phosphorescence of benzophenone can be considered exceptional cases: W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969); C. A. Parker, *Chem. Commun.*, 749 (1968).

[17] Th. Förster, *Discuss. Faraday Soc.*, 27, 7 (1959).

[18] H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1965, p 305.

[19] (a) R. Shimada and L. Goodman, *J. Chem. Phys.*, **43**, 2027 (1965); (b) G. Porter and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **264**, 1 (1961).

[20] (a) Table II contains the highest three bonding MO's, namely those within 0.5 eV of the highest. It is necessary to consider all of these since it is not certain which would correspond to the frontier MO in a more exact calculation. Thus it is seen that the extended Hückel MO method, when applied to *tert*-alkyl aromatic derivatives, does not invariably give the highest occupied MO as π, but in cases gives this as σ. This almost certainly does not correspond to reality. This is in contrast to the nontertiary alkyl aromatics considered previously by Hoffmann[20b] where the highest bonding MO was invariably π; (b) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

lowers the energy of the barrier. Hence, to the extent that the diaryl species, for which three-dimensional calculations are available, are even rough models for 1-benzoyl-4-(α-naphthyl)bicyclo[2.2.2]octane (**15**), a rationale for the triplet excitation delocalization is available. However, independent of interpretation, the facility of triplet transfer can be seen to be easier than previously thought.

Experimental Section[21]

Esr Spectra. Tetrahydrofuran, dimethoxyethane, and a 2:1 mixture of tetrahydrofuran–dimethoxyethane were dried and purified according to the methods previously reported.[1] Dimethyl sulfoxide was distilled *in vacuo* from calcium hydride. Sodium–potassium alloy was prepared by pressing freshly cut sodium and potassium (1:4 weight ratio) together under nitrogen. The liquid alloy formed on standing. Esr samples using sodium–potassium alloy reduction were prepared on a vacuum line and reduced by the procedure reported earlier.[1] Concentrations were *ca.* 10^{-3} *M*.

Sodium–potassium alloy reduction of 1,4-diphenylbicyclo[2.2.2]octane in 2:1 tetrahydrofuran–dimethoxyethane at −90° gave an esr spectrum consisting of five doublets. Simulation of the spectrum on a Digital Equipment Corporation PDP 8/I computer with a program written in these laboratories[22] using coupling constants of 4.66 G for four equivalent hydrogens and 1.78 G for one hydrogen gave the same spectrum.

Similar reduction of 1,4-bis(*p*-nitrophenyl)bicyclo[2.2.2]octane in the same solvent at 25° produced a yellow solution which gave a spectrum consisting of three triplets of triplets, corresponding to splitting from one nitrogen atom and two sets of two hydrogens, superimposed upon a broad peak from a paramagnetic solid which precipitated from the solution. A sample tube with two side arms was used for the reduction in dimethyl sulfoxide with potassium *tert*-butoxide.[10] The sample was placed in one side arm and the potassium *tert*-butoxide in the other. The solvent was placed in the tube and degassed *in vacuo* by four freeze–thaw cycles, and the tube was sealed. Inversion of the sample tube at room temperature gave a deep red solution almost immediately whose esr spectrum was very similar to the spectrum from the sodium–potassium alloy reduction, but the broad peak from the paramagnetic solid was absent.

1,4-Bis(*p*-cyanophenyl)bicyclo[2.2.2]octane was reduced with sodium–potassium alloy at −90° in tetrahydrofuran, dimethoxyethane, and a 2:1 mixture of tetrahydrofuran–dimethoxyethane. In all three solvents, the spectrum could be analyzed as a major splitting from two equivalent hydrogens and a smaller splitting from one nitrogen. The coupling constants changed slightly on changing solvent, as shown in Table I.

Emission Spectra. Hydrocarbon solvents were purified by passing them through a silver nitrate–alumina column according to the method of Murray and Keller.[23] Cyclohexane was used for fluorescence and a 4:1 mixture of methylcyclohexane–isopentane for phosphorescence. Ultraviolet spectra of pivalophenone and 1-methylnaphthalene indicated that 95% of the light at 295 nm should be absorbed by the naphthyl moiety in 1-benzoyl-4-(α-naphthyl)bicyclo[2.2.2]octane, while 100% of the light at 340–350 nm should be absorbed by the benzoyl chromophore. The uv spectrum of 1-benzoyl-4-(α-naphthyl)bicyclo[2.2.2]octane was quite similar to the sum of the spectra of the two model compounds, with slightly enhanced extinction coefficients.

The emission spectra were run on an Aminco Kiers spectrophosphorimeter with 2.5 nm resolution. Phosphorescence spectra were run using a rotating shutter to filter out fluorescence. In order to use the narrowest possible slits to obtain selective excitation of each chromophore, 10–20 sweeps were collected using the above computer and a time-averaging program written in these laboratories.[22] The spectra were normalized to a constant sensitivity and relative intensities proved meaningful with a 5% error due to lamp fluctuations.

A solution of 1-benzoyl-4-(α-naphthyl)bicyclo[2.2.2]octane, 0.0002 *M* in cyclohexane, on excitation at 295 nm gave a fluorescence peak at 330 nm which was only 1% as intense as the fluorescence obtained from a 1:1 mixture of 1-methylnaphthalene and pivalophenone at the same concentration.

A 0.001 *M* solution of 1-benzoyl-4-(α-naphthyl)bicyclo[2.2.2]octane in 4:1 methylcyclohexane–isopentane glass in liquid nitrogen gave phosphorescence emission extending from 460 to 570 nm upon irradiation at 350 nm. No emission was observed at a shorter wavelength than 460 nm. This spectrum was identical with a spectrum obtained from 1-methylnaphthalene under the same conditions but with excitation at 295 nm. The spectrum at 0.0001 *M* was unchanged except for intensity. Similar irradiation at 350 nm of a solution of pivalophenone and 1-methylnaphthalene, 0.001 *M* in each, under the same conditions gave phosphorescence emission extending from 380 to 510 nm which showed the same vibrational structure as the spectrum of pivalophenone. An equimolar solution at 0.01 *M* gave the same spectrum, while at 0.1 *M* the emission extended from 380 to 570 nm and showed emission from both compounds.

Extended Hückel Calculations. These calculations were run using a program developed in these laboratories.[24] The following values were used: valence state ionization potential (VSIP) for the hydrogen 1s orbitals, −13.6 eV; hydrogen 1s Slater exponent, 1.000; carbon 2s VSIP, −21.01 eV; carbon 2p VSIP, −11.27 eV; carbon Slater exponent, 1.625; C–C single bond distance, 1.54 Å; aromatic C–C distance, 1.395 Å; aliphatic C–H distance, 1.107 Å; aromatic C–H distance, 1.084 Å; C–CN distance, 1.44 Å; and C–N triple bond distance, 1.158 Å. It was found necessary to use coordinates accurate to eight significant figures to ensure proper symmetry in the MO's.

γ-Acetyl-γ-phenylpimelonitrile. This compound was prepared by the method of Bruson and Riener.[25] A 33.5-g (0.250 mol) sample of 1-phenylpropan-2-one gave 40.0 g (0.167 mol, 67%) of γ-acetyl-γ-phenylpimelonitrile, mp 109–111° (lit.[25] 109–110°).

γ-Acetyl-γ-phenylpimelic Acid. This compound was also prepared by the method of Bruson and Riener.[25] A sample of 20.0 g (0.083 mol) of γ-acetyl-γ-phenylpimelonitrile gave 16.5 g (0.059 mol, 71%) of γ-acetyl-γ-phenylpimelic acid, mp 170.5–172.5° (lit.[25] 171–172°).

4-Acetyl-4-phenylcyclohexanone. The procedure of Colonge and Vuillemet[26] was followed. It was found that by using an oil-heated (*ca.* 65°) distillation head, without condenser, for distillation of the product as formed, one could prevent the product from solidifying and plugging the system before reaching the receiver flask. A 20.0-g (0.072 mol) sample of γ-acetyl-γ-phenylpimelic acid gave 7.9 g (0.036 mol, 50.6%) of 4-acetyl-4-phenylcyclohexanone, mp 81–82° (lit.[26] 78°).

4-Methoxy-1-phenylbicyclo[2.2.2]octan-2-one. The method of Morita and Kobayashi[6] was used for the preparation of this compound. Thus, 6.56 g (0.0304 mol) of 4-acetyl-4-phenylcyclohexanone gave 5.40 g (0.0235 mol, 77.5%) of 4-methoxy-1-phenylbicyclo[2.2.2]octan-2-one, mp 82.5–83° (lit.[6] 82.5–83.5°).

1-Methoxy-4-phenylbicyclo[2.2.2]octane. A mixture of 50.0 g (0.217 mol) of 1-phenyl-4-methoxybicyclo[2.2.2]octan-2-one, 500 ml of diethylene glycol, 42.0 g (85%, 0.636 mol) of potassium hydroxide, and 28.0 ml (29.0 g, 0.58 mol) of hydrazine hydrate was refluxed for 1 hr. The reaction flask was set up for distillation and the temperature was gradually raised to 200–210° while a few milliliters of distillate (bp *ca.* 110°) were removed over a 3-hr period. The cooled reaction mixture was then poured into 2 l. of water and was ether extracted. The combined extracts were washed with water, dried, and concentrated to give 43.5 g (92.4%) of 1-methoxy-4-phenylbicyclo[2.2.2]octane, mp 37.5–38.5°. The analytical sample was distilled, bp 110° (0.5 mm), through a 6-in. Vigreux column, mp 37.5–38.0°. The spectral data were: ir (KBr) 3.40, 6.30, 6.90, 7.55, 8.32, 8.60, 9.10, 9.68, 9.78, 13.15, and 14.35 μ; nmr ($CDCl_3$) τ 2.73 (broad s, 5 H, arom), 6.80 (s, 3 H, OCH_3), and 8.13 (pseudo s, 12 H, CH_2's).

Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 82.99; H, 9.23.

1-Chloro-4-phenylbicyclo[2.2.2]octane. To an ice-cooled stirred mixture of 2.87 g (0.0133 mol) of 1-methoxy-4-phenylbicyclo[2.2.2]octane and 5.20 ml (8.50 g, 0.0714 mol) of thionyl chloride was added slowly 2.50 ml (5.65 g, 0.0217 mol) of stannic chloride. After 0.5 hr the ice bath was removed, and the mixture was stirred for an additional 3 hr. The mixture was cooled, and 20 ml of water

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[21] All melting points were run on a hot stage and are corrected.

[22] (a) R. D. McKelvey and H. E. Zimmerman, unpublished results; (b) R. D. McKelvey, Ph.D. Thesis, University of Wisconsin, 1971.

[23] E. C. Murray and R. N. Keller, *J. Org. Chem.*, **34**, 2234 (1969).

[24] H. E. Zimmerman and T. W. Flechtner, unpublished results.

[25] H. A. Bruson and T. W. Riener, *J. Amer. Chem. Soc.*, **64**, 2850 (1942).

[26] J. Colonge and R. Vuillemet, *Bull. Soc. Chim. Fr.*, 2235 (1961).

was slowly added (foaming). The mixture was poured into an additional 60 ml of water and was ether extracted. The combined extracts were washed with 5% sodium bicarbonate and then with water, dried with sodium sulfate, and concentrated *in vacuo*. The product was sublimed at 110° (0.5 mm) and recrystallized from hexane to give 0.792 g (27.1%) of 1-chloro-4-phenylbicyclo[2.2.2]octane, mp 88.5–89.5°. The spectral data were: ir (KBr) 3.40, 3.48, 6.22, 6.67, 6.90, 7.38, 7.50, 7.95, 8.61, 9.40, 9.96, 10.16, 11.34, 12.06, 13.12, 14.84, and 15.60 μ; nmr ($CDCl_3$) τ 2.77 (s, 5 H, arom) and 7.93 (broad s, 12 H, CH_2's).

Anal. Calcd for $C_{14}H_{17}Cl$: C, 76.17; H, 7.76; Cl, 16.06. Found: C, 76.39; H, 7.60; Cl, 16.00.

1,4-Diphenylbicyclo[2.2.2]octane. A solution of 374 mg (1.69 mmol) of 1-chloro-4-phenylbicyclo[2.2.2]octane in 2.50 ml of dry benzene was added to a stirred, refluxing mixture of 101 mg (0.63 mmol) of ferric chloride in 2.50 ml of dry benzene over 10 min. The mixture was refluxed for 3 hr, cooled, and poured onto *ca.* 15 g of an ice–concentrated hydrochloric acid mixture. Benzene was added and the organic layer was separated. The aqueous layer was benzene extracted and the extracts were dried with calcium chloride, filtered through sintered glass, and concentrated *in vacuo*. The residue was sublimed at 160° (1–2 mm) and recrystallized from hexane–benzene and from ethanol to give 150 mg (35.7%) of 1,4-diphenylbicyclo[2.2.2]octane, mp 207–209°. The spectral data were: ir (KBr) 3.24, 3.31, 3.40, 3.49, 6.24, 6.67, 6.92, 9.96, 10.06, 11.12, 12.20, 13.24, and 14.35 μ; nmr ($CDCl_3$) τ 2.75 (s, 10 H, arom) and 8.03 (s, 12 H, CH_2's).

Anal. Calcd for $C_{20}H_{22}$: C, 91.55; H, 8.45. Found: C, 91.49; H, 8.30.

1,4-Bis(*p*-nitrophenyl)bicyclo[2.2.2]octane. A mixture of 2.80 ml of sulfuric acid, 0.60 ml of water, 1.70 ml (27.1 mmol) of nitric acid, and 960 mg (3.66 mmol) of 1,4-diphenylbicyclo[2.2.2]octane was stirred under nitrogen for 2 hr at 50–53°. The mixture was poured into ice water and was chloroform extracted. The extracts were washed with water, 5% sodium carbonate, and water, dried with sodium sulfate, and concentrated. The product was recrystallized from benzene to give 0.383 g (29.8%) of 1,4-bis(*p*-nitrophenyl)bicyclo[2.2.2]octane, mp 327.5–328.5° dec. The spectral data were: ir (KBr) 3.26, 3.42, 3.51, 6.30, 6.65, 7.48, 9.04, 11.90, 13.31, and 14.35 μ; nmr ($CDCl_3$) τ 2.20 (AB, $\delta_A - \delta_B$ = 0.65 ppm, 8 H, arom, J_{ab} = 9 Hz) and 7.97 (s, 12 H, CH_2's).

Anal. Calcd for $C_{20}H_{20}N_2O_4$: C, 68.17; H, 5.72; N, 7.95. Found: C, 68.36; H, 5.72, N, 7.80.

1,4-Bis(*p*-bromophenyl)bicyclo[2.2.2]octane. To a stirred solution of 1.500 g (5.72 mmol) of 1,4-diphenylbicyclo[2.2.2]octane in 75 ml of carbon tetrachloride was added 65 mg of iron powder and a solution of 0.58 ml (1.81 g, 11.3 mmol) of bromine in 50 ml of carbon tetrachloride. The mixture was refluxed with stirring for 1.3 hr, by which time the bromine color was gone. The mixture was poured into 1% aqueous sodium borohydride. The aqueous layer was chloroform extracted and the combined organic phases were washed with water, dried with sodium sulfate, concentrated, and recrystallized from chloroform to give 1.43 g (59.5%) of 1,4-bis(*p*-bromophenyl)bicyclo[2.2.2]octane, mp >360°. The spectral data were: ir (KBr) 3.43, 3.51, 6.76, 7.20, 9.08, 9.40, 9.90, 10.10, 12.35, 14.06, and 14.29 μ; nmr (CS_2) τ 2.72 (AB, $\delta_A - \delta_B$ = 0.17 ppm, 8 H, arom, J_{ab} = 9 Hz) and 8.06 (s, 12 H, CH_2's).

Anal. Calcd for $C_{20}H_{20}Br_2$: C, 57.16; H, 4.80; Br, 38.04. Found: C, 56.79; H, 5.15; Br, 38.06.

1,4-Bis(*p*-cyanophenyl)bicyclo[2.2.2]octane. A stirred mixture of 496 mg (1.18 mmol) of 1,4-bis(*p*-bromophenyl)bicyclo[2.2.2]octane, 440 mg (4.91 mmol) of cuprous cyanide, and 8.0 ml of *N*-methylpyrrolidone was heated at 195–200° for 12.5 hr. The mixture was cooled, poured into 150 ml of benzene, and extracted with 7.5% (w/v) aqueous ethylenediamine until no violet color formed in the aqueous layer. The organic solution was washed with water, dried with sodium sulfate, treated twice with Norit, concentrated, and recrystallized from benzene to give 201 mg (54.5%) of 1,4-bis(*p*-cyanophenyl)bicyclo[2.2.2]octane, mp 280–281°. The spectral data were: ir (KBr) 3.40, 3.50, 4.51 (C≡N), 6.24, 6.68, 7.68, 8.50, 9.83, 10.05, 10.50, and 12.10 μ; nmr ($CDCl_3$) τ 2.40 (AB, $\delta_A - \delta_B$ = 0.17 ppm, 8 H, arom, J_{ab} = 9 Hz) and 8.01 (s, 12 H, CH_2's).

Anal. Calcd for $C_{22}H_{20}N_2$: C, 84.58; H, 6.45; N, 8.97. Found: C, 84.75; H, 6.71; N, 8.66.

1-(α-Naphthyl)propan-2-one. An ether solution of dimethylcadmium was prepared in the usual manner[27] starting from 20.0 g (0.824 g-atom) of magnesium turnings, 1 equiv of methyl bromide, and 150 g (0.82 mol) of anhydrous cadmium chloride. The solution gave a negative Gilman test[28] for Grignard reagent. A solution of α-naphthylacetyl chloride was prepared by refluxing a mixture of 50.0 g (0.269 mol) of α-naphthylacetic acid and 30.0 ml (49.0 g, 0.412 mol) of thionyl chloride for 1.5 hr. Excess thionyl chloride was removed by distillation and codistillation with dry benzene. Sufficient benzene (50 ml) was then added to give a homogeneous solution. The solution of α-naphthylacetyl chloride was added to the stirred dimethylcadmium solution during 30 min, and the mixture was refluxed for an additional 35 min. Sulfuric acid (300 ml, 1.8 *M*) was added slowly to the cooled mixture. The aqueous layer was ether extracted and the extract was added to the organic layer, which was then washed with 5% sodium carbonate and water, dried with sodium sulfate, concentrated, and distilled to give 32.9 g (66.5%) of 1-(α-naphthyl)propan-2-one, bp 121–126° (0.75 mm). The spectral data were: ir (neat) 3.28, 3.44, 5.85, (C=O), 6.26, 6.62, 7.07, 7.17, 7.39, 7.60, 8.14, 8.60, 9.80, 12.75, 12.95, and 13.62 μ; nmr (CS_2) τ 2.12–2.93 (m, 7 H, arom), 6.18 (s, 2 H, CH_2), and 8.22 (s, 3 H, CH_3).

The semicarbazone was prepared and melted at 189.5–190.5°.

Anal. (semicarbazone) Calcd for $C_{14}H_{15}N_3O$: C, 69.69; H, 6.27; N, 17.42. Found: C, 69.76; H, 6.40; N, 17.37.

γ-Acetyl-γ-(α-naphthyl)pimelonitrile. To a stirred, ice-cooled solution of 30.0 g (0.162 mol) of 1-(α-naphthyl)propan-2-one in 50 ml of *tert*-butyl alcohol was added 3.90 ml of 40% benzyltrimethylammonium methoxide, followed by 17.2 g (0.324 mol) of acrylonitrile over 20 min. The mixture was stirred at room temperature for 3.5 hr, concentrated, and triturated with 75 ml of hot methanol to give a product which was filtered, washed with cold methanol, and recrystallized from ethyl alcohol containing a small amount of chloroform to give 23.0 g (49%) of γ-acetyl-γ-(α-naphthyl)pimelonitrile, mp 138.5–140.0°. The spectral data were: ir (KBr) 3.40, 4.46 (C≡N), 5.90 (C=O), 7.02, 7.38, 7.92, 8.12, 8.54, 8.63, 9.25, 10.35, 12.49, 12.80, and 13.07 μ; nmr ($CDCl_3$) τ 1.90–2.75 (m, 7 H, arom), 7.15–8.10 (m, 8 H, CH_2's), and 8.11 (s, 3 H, CH_3).

Anal. Calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.66; H, 6.28; N, 9.43.

γ-Acetyl-γ-(α-naphthyl)pimelic Acid. A mixture of 5.45 g (0.0188 mol) of γ-acetyl-γ-(α-naphthyl)pimelonitrile, 25 ml of water, and 2.3 g (0.058 mol) of sodium hydroxide was refluxed for 25 hr. The mixture was acidified with 12 ml of 6 *N* hydrochloric acid, and the product was filtered, digested in hot water, separated by filtration, dried, and recrystallized from ethyl alcohol to give 5.45 g (90.0%) of γ-acetyl-γ-(α-naphthyl)pimelic acid, mp 258–260°. The spectral data were: ir (KBr) 3.40, 5.90 (C=O), 6.24, 6.62, 7.06, 7.62, 8.19, 8.56, 9.20, 10.12, 10.70, 11.58, 12.47, 12.85, 13.42, 14.35, 15.00, and 15.70 μ; nmr (DMSO-d_6) τ 1.90–2.76 (m, 7 H, arom), 7.36–8.12 (m, 8 H, CH_2's), and 8.23 (s, 3 H, CH_3).

Anal. Calcd for $C_{19}H_{20}O_5$: C, 69.50; H, 6.14. Found: C, 69.13; H, 6.32.

4-Acetyl-4-(α-naphthyl)cyclohexanone. A mixture of 5.010 g (0.0153 mol) of γ-acetyl-γ-(α-naphthyl)pimelic acid and 20.0 ml of acetic anhydride was refluxed for 1.5 hr. The excess acetic anhydride and acetic acid were distilled. Vacuum was applied, the temperature was raised to 225°, and the product was distilled using an oil-heated (150–160°) distillation head to prevent product solidification in the distillation apparatus, bp 200–205° (0.5–2.0 mm). The glassy product was powdered and recrystallized from methanol to give 0.860 g (21.0%) of 4-acetyl-4-(α-naphthyl)cyclohexanone, mp 147–148°. The spectral data were: ir (KBr) 3.38, 5.89 (C=O), 6.24, 6.62, 6.90, 7.07, 7.15, 7.40, 8.20, 8.32, 8.46, 8.55, 8.62, 8.88, 9.72, 10.30, 10.68, 11.03, 11.30, 12.42, 12.72, 13.35, and 14.80 μ; nmr ($CDCl_3$) τ 1.90–2.75 (m 7 H, arom), 7.00–7.90 (m, 8 H, CH_2's), and 8.13 (s, 3 H, CH_3).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.46; H, 7.05.

1-(α-Naphthyl)-4-methoxybicyclo[2.2.2]octan-2-one. A mixture of 24.5 g (0.092 mol) of 4-acetyl-4-(α-naphthyl)cyclohexanone, 200 ml of methanol, 32 ml of 25% (w/v) hydrogen chloride in methanol, and 34.5 ml of trimethyl orthoformate was refluxed for 1.3 hr. The solvent was distilled and the residue was dissolved in chloroform, extracted with 5% sodium carbonate and water, dried, and concentrated. The crude product was recrystallized from benzene–hexane to give 19.84 g (77%) of 1-(α-naphthyl)-4-

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[27] J. Cason, *Chem. Rev.*, **40**, 15 (1947).

[28] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1957, p 269.

methoxybicyclo[2.2.2]octan-2-one, mp 169–169.5°. The spectral data were: ir (KBr) 3.28, 3.40, 3.54, 5.84 (C=O), 6.25, 6.88, 7.10, 7.16, 7.49, 8.42, 8.51, 8.79, 9.10, 9.62, 9.88, 10.50, 12.66, 12.95, and 15.12 μ; nmr ($CDCl_3$) τ 1.95–2.82 (m, 7 H, arom), 6.70 (s, 3 H, OCH_3), 7.22 (s, 2 H, CH_2CO), and 7.33–8.42 (m, 8 H, CH_2's).

Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.64; H, 7.18.

1-Methoxy-4-(α-naphthyl)bicyclo[2.2.2]octane. A mixture of 840 mg (3.0 mmol) of 1-(α-naphthyl)-4-methoxybicyclo[2.2.2]octan-2-one, 15 ml of diethylene glycol, 1.3 ml (1.26 g, 25.2 mmol) of hydrazine hydrate, and 840 mg (85%, 15.4 mmol) of potassium hydroxide was refluxed for 1.25 hr. The temperature was raised to 230° while a small amount of distillate, bp *ca.* 110°, was removed. The temperature was maintained at 230° for 8 hr. After cooling overnight, the mixture was poured into 75 ml of water and ether extracted. The extract was washed with water, dried, and concentrated. The residue was crystallized from benzene–hexane (1:1) to give 97 mg of material, mp 160–165°. The mother liquor was evaporated to dryness, and the residue was sublimed (160°, 1 mm). The sublimate was recrystallized from hexane to give 254 mg (31.8%) of 1-methoxy-4-(α-naphthyl)bicyclo[2.2.2]octane, mp 105–106.5°. The spectral data were: ir (KBr) 3.28, 3.42, 3.48, 6.25, 6.64, 6.90, 7.16, 7.40, 8.34, 8.56, 9.16, 9.69, 10.00 12.92, and 13.40 μ; nmr ($CDCl_3$) τ 2.00–2.80 (m, 7 H, arom), 6.78 (s, 3 H, OCH_3), and 7.50–8.58 (symmetric m, 12 H, CH_2's).

Anal. Calcd for $C_{19}H_{22}O$: C, 85.67, H, 8.32. Found: C, 85.67; H, 8.40.

1-Bromo-4-(α-naphthyl)bicyclo[2.2.2]octane. A mixture of 3.979 g (0.015 mol) of 1-methoxy-4-(α-naphthyl)bicyclo[2.2.2]octane, 40 ml of acetic acid, and 40 ml of 48% hydrobromic acid was refluxed for 3.5 hr. The mixture was poured into 200 ml of water and benzene extracted. The extracts were washed with water, with 5% sodium carbonate, and with water, treated with Norit, dried, concentrated, and recrystallized from benzene–hexane to give 3.704 g of impure material. This was chromatographed in three batches on a 3 × 95 cm silica gel (Grace 950, 60–200 mesh) column slurry packed with 5% ether–hexane; 500-ml fractions were taken, and the product was in the third fraction. Recrystallization from benzene–hexane gave 2.58 g (54.9%) of 1-bromo-4-(α-naphthyl)bicyclo[2.2.2]octane, mp 165.5–166°. The spectral data were: ir (KBr) 3.30, 3.35, 3.40, 3.49, 6.26, 6.63, 6.90, 7.17, 7.42, 7.79, 8.05, 8.60, 9.93, 10.52, 11.43, 12.21, 12.50, 12.94, and 14.90 μ; nmr ($CDCl_3$) τ 1.65–2.90 (m, 7 H, arom) and 7.65 (pseudo s, 12 H, CH_2's).

Anal. Calcd for $C_{18}H_{19}Br$: C, 68.58; H, 6.07. Found: C, 68.79; H, 5.89.

1-Cyano-4-(α-naphthyl)bicyclo[2.2.2]octane. A mixture of 620 mg (1.97 mmol) of 1-bromo-4-(α-naphthyl)bicyclo[2.2.2]octane, 625 mg (7.10 mmol) of cuprous cyanide, and 12 ml of pyridine was gradually heated to 220° under nitrogen while the pyridine distilled. The temperature was maintained at 220° for 40 hr. A white crystalline solid (174 mg) had sublimed into the neck of the flask. This material was chromatographed on a 3 × 95 cm column of silica gel (Grace 950, 60–200 mesh) slurry packed with 5% ether–hexane. Elution in 250-ml fractions gave: fractions 1–4, 5% ether–hexane, nil; 5–6, 5% ether–hexane, 23.4 mg; 7–12, 5% ether–hexane, nil; 13–18, 8% ether–hexane, nil; 19–25, 12% ether–hexane, 140 mg (27.3%) of 1-cyano-4-(α-naphthyl)bicyclo-[2.2.2]octane, mp 224–226°. The analytical sample was recrystallized from benzene–hexane and had mp 225.5–226°. Extraction of the remainder of the reaction product gave only a small amount of impure product. The spectral data were: ir (KBr) 3.24, 3.30, 3.36, 3.40, 3.49, 4.49 (C≡N), 6.26, 6.63, 6.75, 6.89, 7.17, 7.46, 7.83, 9.28, 9.80, 10.40, 11.85, 12.47, 12.92, and 15.64 μ; nmr ($CDCl_3$) τ 1.70–2.85 (m, 7 H, arom) and 7.85 (broad s, 12 H, CH_2's).

Anal. Calcd for $C_{19}H_{19}N$: C, 87.31; H, 7.33. Found: C, 87.50; H, 7.14.

1-Benzoyl-4-(α-naphthyl)bicyclo[2.2.2]octane. A solution of phenylmagnesium bromide was prepared from 0.32 g (0.0132 g-atom) of magnesium, 2.0 ml (3.0 g, 0.019 mol) of bromobenzene, and 25 ml of dry ether. Benzene (30 ml) was added and the ether was distilled. A solution of 0.274 g (0.00105 mol) of 1-cyano-4-(α-naphthyl)bicyclo[2.2.2]octane in 10 ml of benzene was added and the mixture was refluxed for 2.5 hr. Water (2 ml) was added slowly to the cooled mixture, followed by 35 ml of concentrated hydrochloric acid. The mixture was heated to distill the benzene, after which 35 ml of acetic acid was added to increase solubility, and the mixture was refluxed for 6 hr. The cooled mixture was poured into 200 ml of water and was benzene extracted. The extract was washed with water, 5% sodium carbonate, and again with water and dried, and the benzene was distilled. Excess bromobenzene was removed *in vacuo*, leaving 0.420 g of crude product. Purification was effected by chromatography on a 3 × 95 cm silica gel column slurry packed with 3% ether–hexane. Elution in 250-ml fractions gave: fractions 1–4, 3% ether–hexane, nil; 5–6, 3% ether–hexane, trace; 7–11, 5% ether–hexane, nil; 12–19, 5% ether–hexane, 0.327 g. Fractions 13–17 (0.230 g) were combined and recrystallized from benzene–hexane to give 0.185 g (56.5%) of cubic crystals, mp 138–139°. All subsequent recrystallizations gave needles of 1-benzoyl-4-(α-naphthyl)bicyclo[2.2.2]-octane, mp 159–159.5°. The spectral data were: ir (KBr) 3.28, 3.42, 3.49, 5.97 (CO), 6.26, 6.37, 6.65, 6.86, 6.95, 7.17, 7.47, 7.80, 7.95, 8.09, 8.55, 9.33, 9.91, 10.35, 10.69, 10.95, 11.55, 12.50, 12.92, 13.68, 14.36, and 15.22 μ; nmr ($CDCl_3$) τ 2.05–2.85 (m, 12 H arom) and 7.82 (s, 12 H, CH_2's); mass spectrum *m/e* 105 (PhCO) and 340 parent; uv (cyclohexane) 256 min (ϵ 3660), 273 max (ϵ 7900), 276 min (ϵ 7250), 283 max (ϵ 9600), 294 sh (ϵ 6400), 313 max (ϵ 660), and 350 nm tail (ϵ 60).

Anal. Calcd for $C_{25}H_{24}O$: C, 88.19; H, 7.11. Found: C, 88.01; H, 7.09.

The uv spectrum of a 1:1 mixture of pivalophenone and 1-methylnaphthalene was: 256 min (ϵ 3750), 273 max (ϵ 7000), 276 min (ϵ 6300), 283 max (ϵ 7600), 294 sh (ϵ 4930), 313 max (ϵ 600), and 350 nm tail (ϵ 43).

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