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Thermal Transformations of *cis*-1,2-Dibenzoylalkenes

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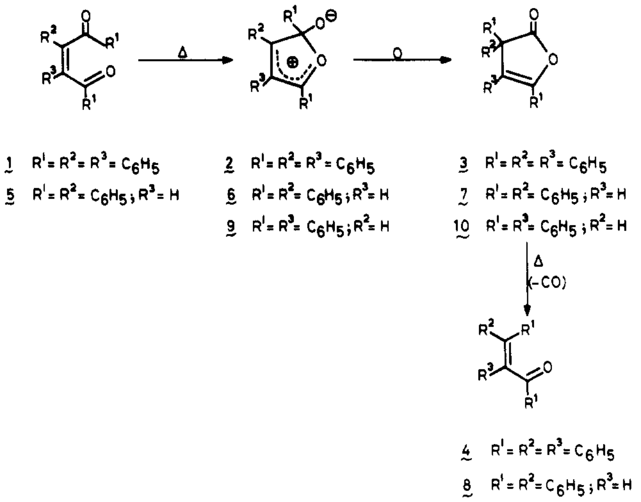
Thermal transformations of a few *cis*-1,2-dibenzoylalkenes such as 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (**12**), 2,3-dibenzoyl-7-oxabicyclo[2.2.1]hept-2-ene (**16**), and 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (**19**) have been examined. Thermolysis of **12** gave 2-benzoyl-3-phenylbicyclo[2.2.2]oct-2-ene (**14**) through the loss of CO from the lactone precursor **13**. The thermolysis of **16**, on the other hand, gave 3,4-dibenzoylfuran (**17**), through a fragmentation reaction. In contrast, the thermolysis of **19** gave 2-*endo*-3-*exo*-dibenzoylbicyclo[2.2.1]heptane (**20**), probably through a disproportionation reaction. Ab initio molecular orbital calculations were made on model compounds representing the conversion of *cis*-1,2-dibenzoylalkenes to the corresponding lactones to determine whether mechanisms involving intermediates such as the bicyclic structure **23**, the dipolar structure **25**, and the diradical structure **28** (Scheme IV) are feasible under thermal conditions. The bicyclic structure **23** is found to be easily accessible, lying between the starting material and final product in energy. Any mechanism involving the dipolar intermediate **25** seems to be less likely. The intermediate **28**, which is geometrically similar to **25** but is of diradical rather than dipolar nature, is found to be comparable in energy to the starting material. It is concluded that the actual mechanism may then involve **23**, **28**, or perhaps even both of these.

Numerous examples of the thermal transformations of heterohexa-1,3,5-trienes leading to five-membered heterocycles are reported in the literature.[3] As early as 1872, Zinin had reported that the thermolysis of *cis*-1,2-dibenzoylstilbene (**1**) leads to an isomeric lactone.[4] Subsequent studies by Japp and Klingemann[5] have shown that the product isolated by Zinin in the thermolysis of **1** is actually the decarbonylated derivative **4** and not the isomeric lactone **3** (Scheme I). These authors have shown that the dry distillation of **1** under reduced pressure leads initially to the lactone **3**, which subsequently undergoes decarbonylation to give **4** under the reaction conditions. They had further shown that a substrate such as 1,2,4-triphenylbut-2-ene-1,4-dione (**5**) undergoes thermal isomerization to give exclusively 2,2,4-triphenylbut-3-enolide (**7**) and none of the isomeric 2,3,4-triphenylbut-3-enolide (**10**). The structure of **7** was further confirmed through its conversion to the enone **8** on heating. The preferential formation of the lactone **7** in the thermal transformation of **5** has been rationalized in terms of the greater stability of the dipolar intermediate **6**, when compared to the corresponding intermediate **9**, in the alternative route which will lead to the lactone **10** (Scheme I).[5,6] It may be mentioned in this connection that the reported[7] thermal rearrangement of tetraphenyl-*p*-dioxin to give the lactone **3** has been shown to involve *cis*-1,2-dibenzoylstilbene (**1**) as an intermediate which then undergoes further transformation to give the lactone **3**.[8,9]

Scheme I



It has been reported recently that several *cis*-1,2-dibenzoylalkenes which are susceptible to thermal fragmentations do not undergo rearrangement to give the corresponding lactones.[6] Thus, it has been observed that the thermolysis of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**18**), for example, leads to cyclopentadiene through a retro-Diels–Alder fragmentation pathway. Similar fragmentations have been observed in the case of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**15**) and 9,10-dihydro-11,12-diobenzoyl-9,10-etheneanthracene. The thermolysis of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (**11**), on the other hand, gave a nearly quantitative yield of 1,2-dibenzoylbenzene, presumably formed through the loss of the elements of ethylene. In contrast, the thermolysis of 1,4-diphenyl-2,3-dibenzoyl-1,4-epoxynaphthalene gave a mixture of 1,3-diphenylisobenzofuran and 1,2-dibenzoylbenzene.

Here we report the thermal transformations of a few representative *cis*-dibenzoylalkenes of the bicyclo[2.2.1]heptene and bicyclo[2.2.2]octene series which have structural features which would not favor the retro-Diels–Alder mode of fragmentation over the expected rearrangement. In addition, the mechanism of the thermal rearrangement of *cis*-1,2-dibenzoylalkenes to the corresponding lactones has been examined by using theoretical calculations.

Results and Discussion

The *cis*-dibenzoylalkenes that we have examined in this connection include 2,3-dibenzoylbicyclo[2.2.2]oct-2-ene (**12**), 2,3-dibenzoyl-7-oxabicyclo[2.2.1]hept-2-ene (**16**), and 2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (**19**). These starting alkenes themselves were prepared from the corresponding diene precursors through catalytic hydrogenation under controlled conditions. Thus, the catalytic hydrogenation

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[3] For a recent survey of the thermal and photochemical transformations of heterohexa-1,3,5-trienes, see M. V. George, A. Mitra, and K. B. Sukumaran, submitted for publication in *Angew. Chem., Int. Ed. Engl.*

[4] N. Zinin, *Chem. Ber.*, **5**, 1104 (1872).

[5] F. R. Japp and F. Klingemann, *J. Chem. Soc.*, 662 (1890).

[6] S. Lahiri, V. Dabral, M. P. Mahajan, and M. V. George, *Tetrahedron*, **33**, 3247 (1977).

[7] A. H. Blatt, *J. Org. Chem.*, **15**, 869 (1950).

[8] S. Lahiri, V. Dabral, and M. V. George, *Tetrahedron Lett.*, 2259 (1976).

[9] S. Lahiri, V. Dabral, V. Bhat, E. D. Jemmis, and M. V. George, *Proc. Indian Acad. Sci., Sect. A*, **86A**, 1 (1977).

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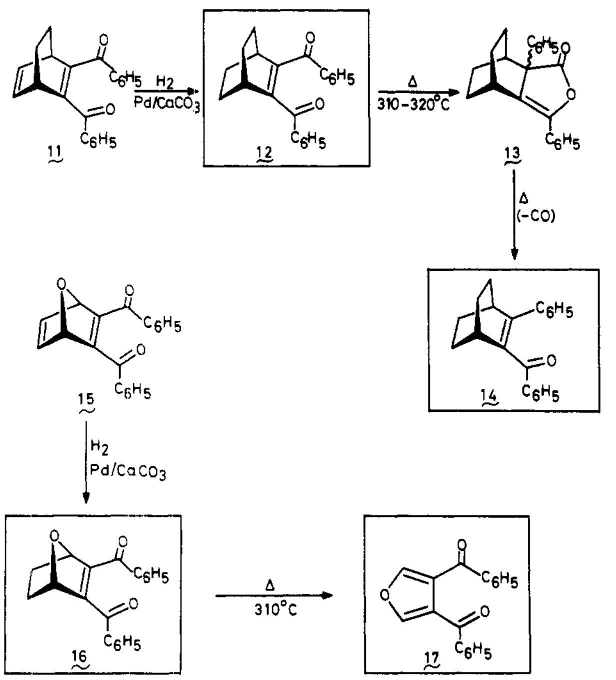
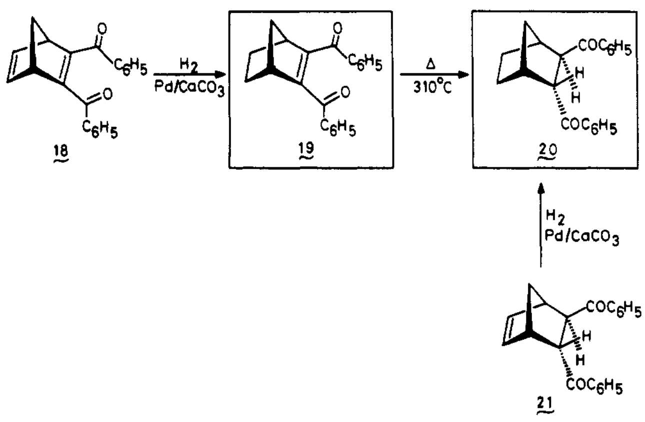
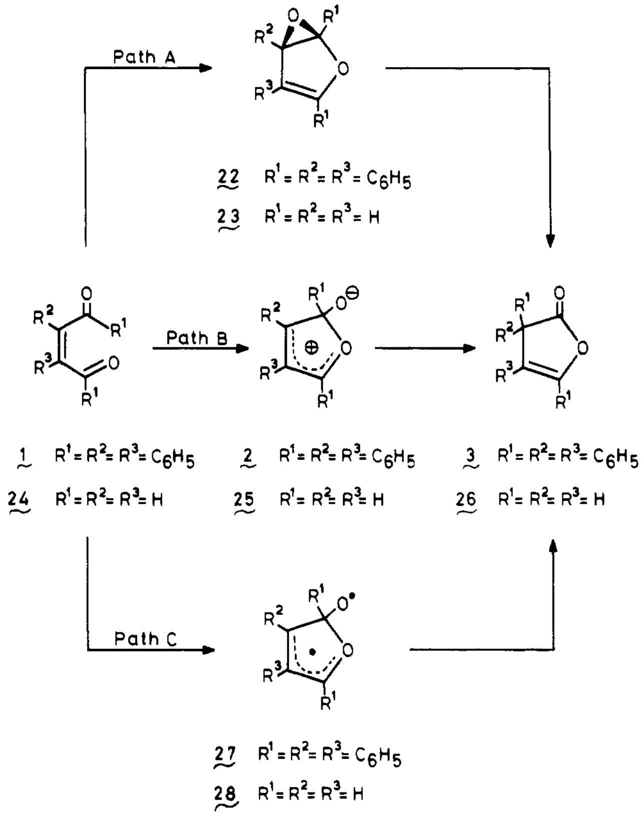
Scheme II



Scheme III



Scheme IV



of 2,3-dibenzoylbicyclo[2.2.2]octa-2,5-diene (**11**) over 5% Pd on $CaCO_3$ in ethyl acetate gave an 89% yield of **12**. Under similar conditions, 2,3-dibenzoyl-7-oxabicyclo-[2.2.1]hepta-2,5-diene (**15**) and 2,3-dibenzoylbicyclo-[2.2.1]hepta-2,5-diene (**18**) gave the corresponding alkenes, **16** (90%) and **19** (93%), respectively. The structures of **12**, **16**, and **19** were established on the basis of analytical results and spectral data (see Experimental Section).

Thermolysis of **12** around 310–320 °C for 1 h gave a 44% yield of a product identified as 2-benzoyl-3-phenylbicyclo[2.2.2]oct-2-ene (**14**, Scheme II). The formation of **14** in this reaction may be rationalized in terms of the initial rearrangement of **12** to the isomeric lactone **13**, followed by loss of CO from **13** under the reaction conditions. It may be mentioned in this connection that the photolysis of **12** leads to different products, depending on the nature of the solvent and the reaction conditions, and the formation of these products has been rationalized in terms of diradical intermediates.[10]

In contrast to the thermal rearrangement of **12**, the thermolysis of **16** gives rise to fragmentation products. Thus, heating of **16** around 310 °C in a sealed tube for 1 h gave a 74% yield of 3,4-dibenzoylfuran (**17**), presumably formed through a fragmentation mode, with the loss of the elements of ethylene (Scheme II). The thermolysis of **19**, on the other hand (Scheme III), gave a 30% yield of a product identified as 2-*endo*-3-*exo*-dibenzoylbicyclo-[2.2.1]heptane (**20**). The structure of **20** was confirmed through comparison with a sample prepared by a separate procedure involving the hydrogenation of 2-*endo*-3-*exo*-dibenzoylbicyclo[2.2.1]hept-5-ene (**21**). The formation of **20** in the thermolysis of **19** may occur through a disproportionation reaction, perhaps involving radical intermediates. It is interesting to note that none of the expected rearrangement products could be isolated from this reaction.

Mechanism of the Thermal Rearrangement of *cis*-1,2-Dibenzoylalkenes. From the examples reported in the literature and on the basis of the present studies, it is reasonable to assume that one of the major modes of transformation of appropriately substituted *cis*-1,2-dibenzoylalkenes is their thermal isomerization to the corresponding lactones. If we consider the simple case of the isomerization of **1** to **3**, for example, it is evident that several alternative pathways can be formulated for this transformation (Scheme IV). One conceivable mode would be a possibly concerted cycloaddition[11] (path A) to give the bicyclic intermediate **22**, which can subsequently give rise to **3**, either by a concerted process (dyotropic rearrangement[12]) or through a stepwise pathway. Alternatively, **1** can be directly transformed to the dipolar intermediate **2** (path B), which then can undergo facile rearrangement, leading to **3**. The transformation of **1** to **2** is analogous to the ring–chain tautomerism exhibited by several 1,2-dicarbonyl substrates.[13] A third possible

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(10) S. Lahiri, V. Dabral, S. M. S. Chauhan, E. A. Chakachery, C. Vijaya Kumar, J. C. Scaiano, and M. V. George, submitted for publication in *J. Org. Chem.*

(11) R. B. Woodward and R. Hoffmann "The Conservation of Orbital Symmetry", Academic Press, New York, 1970.

(12) For some examples of 1,2-dyotropic rearrangements, see M. T. Reetz, *Tetrahedron*, **29**, 2189 (1973).

Table I. Conformations of Starting Material 24

	dihedral angle,[a] deg		
structure	C(3)C(2)-C(1)O(1)	C(2)C(3)-C(4)O(2)	rel energy, kcal/mol[b]
24a	180	180	0.0
24b	±90	180	1.7
24c	0	180	7.7
24b	180	±90	1.7
24d	+(−)90	−(+)90	7.3
24f	+(−)90	+(−)90	6.9
24e	0	±90	1.4
24c	180	0	7.7
24e	±90	0	1.4
24g	0	0	109.9

[a] The atom numbering scheme for **24** is C(1)(O(1))-H(1)C(2)H(2)=C(3)H(3)C(4)(O(4))H(4). [b] All energies given relative to −299.5128 au, the calculated energy of **24a**.

pathway for the transformation of **1** would involve its conversion to the diradical intermediate **27** (path C) and the subsequent rearrangement of **27** to **3**. In addition, there may also be the possibility of interconversion of the different intermediates, **22**, **2**, and **27**, before they undergo rearrangement to **3**.

In order to obtain qualitative information about these possible mechanisms, we carried out ab initio molecular orbital calculations on the various structures in Scheme IV. To keep the calculations tractable, we examined only model compounds such as **23–26** and **28**, having all phenyl groups replaced by hydrogen atoms. All computations were made with the GAUSSIAN 70 program package[14] with a minimal STO-3G basis set.[15]

Structure of 24. The conformation of the starting material **24** was investigated by allowing internal rotation about one or both of the C–C single bonds (Table I). Since only qualitative information was being sought, no relaxation of other geometrical parameters from their standard values[16] was considered. The most stable structure was found to have all atoms planar and the two oxygen atoms cis to the respective α-hydrogens (see **24a** in Table I). This, however, cannot be taken as a reasonable model for the actual compound of interest, due to the high steric hindrance that would occur if the terminal hydrogen atoms of the model compounds were replaced by phenyl groups. Keeping such steric considerations in mind, it seems from examination of Table I that something close to structure **24e**, which is calculated to be only 1.4 kcal higher in energy than **24a**, is the most likely conformation of the actual compound **24**. This conformation is also clearly favorable for incipient conversion to the proposed intermediates **23**, **25**, and **28**. Thus, **24e** will be taken to represent the structure of **24**.

The HOMO and LUMO of **24e** are each of approximate π symmetry. The HOMO has bonding contributions at the C=C and the inplane C=O groups, with an additional minor σ contribution parallel to the plane at the out-of-plane oxygen atom. The contributions at the C=C and C=O groups become antibonding in nature in the LUMO.

Structure of 26. Next, we consider the cyclic structure of the final product **26**. For this purpose, all bond lengths were assigned standard values.[16] Considerable investigation indicated that no significant relief of the slightly strained ring bond angles could be obtained by allowing nonplanarity, so calculations were made only on planar structures. Bond angles for atoms exterior to the ring were fixed by steric considerations, i.e., by assuming the atoms to be equidistant from the nearest neighbors of the ring atoms they were bonded to, and the HCH angle in the methylene group was taken to be tetrahedral. This left only the ring bond angles undetermined, and these were fixed by optimization of two ring angles until the lowest energy structure was found.[17] As might be expected, the ring angles were strongly coupled, and several passes were required for complete optimization. Structures several kilocalories lower in energy could still undoubtedly be found by additional optimization of ring bond lengths, but such extensive calculations were not deemed necessary for the present qualitative investigation.

The resulting structure for **26** is calculated to be 49 kcal lower in energy than that for **24e**. The HOMO and LUMO of **26** each have pure π symmetry. The HOMO has significant contributions bonding the C=C group and localized on the ring oxygen atom and an additional smaller contribution at the ketone oxygen atom that is slightly bonding in the C=O region. The LUMO has no more nodes, but the nodes shift to give antibonding character to the C=C and C=O groups and to greatly diminish the amplitude at the ring oxygen atom.

Structure of 23. In order to obtain information about the feasibility of the mechanism labeled path A in Scheme IV, we made calculations on the bicyclic intermediate **23**. Bond lengths and interior bond angles for the oxirane group were taken from another experiment.[18] All other bond lengths were assigned standard values.[16] Bond angles for the hydrogen atoms were determined by steric considerations. Two angles were optimized to fix the (planar) five-membered-ring structure, as was one dihedral angle to determine the tilt of one ring relative to the other.[19] Here again, additional optimization of bond lengths would be expected to lower the energy by a few more kilocalories, but this was not attempted.

The resulting structure for **23** is calculated to be 29 kcal lower in energy than that for **24e** or 20 kcal higher than that for **26**. Thus, somewhat surprisingly, energetics indicate that **23** is a possible intermediate. The HOMO of **23** consists of π functions (with respect to the five-membered ring) bonding the C=C group and on the adjacent oxygen atoms together with a lone-pair-type orbital parallel to the five-membered ring and localized on the oxirane oxygen atom. In the LUMO, the C=C contribution is antibonding, the amplitude at the adjacent oxygen atom is somewhat diminished, and the lone-pair-type contribution on the oxirane oxygen atom is rotated to lie more along a CO bond and has an inverted phase.

Structure of 25. The dipolar structure of **25** is another conceivable intermediate. To investigate this possibility, we made closed-shell SCF calculations at a reasonable assumed geometry having ring bond angles close to the optimized values found for **26**[17] and **23**.[19] The resulting wave function was indeed ionic in character, as indicated by the large dipole moment of 4.9 D. The direction of the

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(13) P. R. Jones, *Chem. Rev.*, **63**, 461 (1963).

(14) W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, *QCPE*, **No. 10**, 236 (1973).

(15) W. J. Hehre, R. W. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(16) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

(17) Optimized interior ring bond angles for **26** were found to be C=C—C = 107.4°, C—C—C = 100.3°, C—C—O = 110.0°, C—O—C = 108.1°, and O—C=C = 114.2°.

(18) W. D. Gwinn and W. I. Levan, *J. Chem. Phys.*, **19**, 676 (1951).

(19) Optimized interior ring bond angles for **23** were found to be C=C—C = 106.1°, C—C—C = 102.7°, C—C—O = 109.7°, C—O—C = 105.4°, and O—C=C = 116.1°. The dihedral angle fixing the tilt of the oxirane ring relative to the five-membered ring was found to be C=C—C—O = −107.6°.

dipole moment vector indicated excess negative charge on the exterior oxygen atom, with the residual positive charge associated with the ring atoms, as expected. The HOMO was of complicated σ–π character. The total energy of **25** was calculated to be 75 kcal above that of **24e**. It was thus not deemed profitable to attempt any geometry optimization on **25**, which would be expected to lower the energy by only a few kilocalories. This single calculation seems sufficient to indicate that path B in Scheme IV is not likely.

Structure of 28. It is also possible that an intermediate having a geometrical structure similar to **25** but having a wave function of diradical rather than dipolar character could be involved, as shown by **28** in path C of Scheme IV. This was investigated with a UHF calculation on a nominal singlet state with an assumed reasonable geometry identical with that taken for **25**. Although convergence to the closed-shell dipolar state **25** was certainly possible in this calculation, the UHF procedure instead located a much more stable open-shell state, **28**. The pure singlet component of this state was determined by spin projection[20] to remove all undesirable spin contamination. The resulting pure singlet wave function was not dipolar in nature, having a calculated dipole moment of only 2.0 D, as compared to 4.9 D for **25**. Calculation of the charge-density natural orbitals[20] showed that the 44 electrons were distributed among 21 orbitals having an occupation number close to 2 (1.93–2.00), two orbitals having an occupation number close to 1 (1.11 and 0.89), and the remaining orbitals having an occupation number near 0 (0.00–0.07). This clearly shows the diradical nature of the singlet component in the UHF wave function[21] of **28**. The two singly occupied "diradical" natural orbitals were both linear combinations of π functions on the ring and a lone-pair-type function on the exterior oxygen atom.

The energy calculated directly for the diradical state of **28** is not too meaningful due to significant spin contamination in the UHF wave function. A rough estimate of the energy of the pure singlet component was obtained by attributing all of the spin contamination to the triplet state[22] and removing the contribution of the latter by taking it weight from the spin-projection analysis[20] and its energy from a separate UHF triplet calculation. Treating the starting material **24e** on the same basis for comparison,[23] we found the UHF "singlet energy" of **28** to be only about 8 kcal/mol higher than the energy of **24e**. While this result should not be taken as quantitative, it seems sufficient to at least draw the conclusions that a diradical singlet state for **28** is considerably more stable than the corresponding dipolar state of **25** and that **28** is energetically easily accessible from **24e**. Thus, path C should be considered as a possible mechanism.

Summary of Calculations. Conversion of **24** to **26** is highly exothermic, the calculations indicating a release of about 50 kcal/mol. While a comprehensive analysis of the mechanism must await studies of substituent effects and of transition states, among other things, some important conclusions can be drawn from the present limited studies. On the basis of the relative energies of the various intermediates **23**, **25**, and **28**, we feel that the dipolar intermediate **25**, arising through path B, is unlikely to be involved in the thermal transformation of **24** to **26**. On the other hand, both path A and path C, leading to the bicyclic intermediate **23** and the diradical intermediate **28**, respectively, are possible pathways in this transformation. It is also possible that the reaction proceeds initially through path C to give **28**, which could then be converted to **23** and finally to **26**. This points the direction for further work in clarifying details of the mechanism.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on either a Perkin-Elmer Model 137 or Model 521 infrared spectrometer. NMR traces were recorded on either a Varian A-60 or HA-100 NMR spectrometer using tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-6E, single-focusing mass spectrometer at 70 eV.

Starting Materials. 2,3-Dibenzoylbicyclo[2.2.2]octa-2,5-diene (**11**,[6] mp 153 °C), 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**15**,[6] mp 122–123 °C), 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**18**,[6,24] mp 144 °C), and 2-*endo*-3-*exo*-dibenzoylbicyclo[2.2.1]hept-5-ene (**21**,[25] mp 80 °C) were prepared by reported procedures. The petroleum ether used was the fraction with a boiling point of 60–80 °C.

2,3-Dibenzoylbicyclo[2.2.2]oct-2-ene (12). A solution of 3.14 g (0.01 mol) of **11** in 150 mL of ethyl acetate was hydrogenated over 5% Pd on $CaCO_3$ at room temperature and 10 psi of H_2 for 15 min. Removal of the catalyst and evaporation of the solvent under reduced pressure gave a product which was recrystallized from ethyl acetate to give 2.8 g (89%) of **12**: mp 145 °C; IR ν_{max} (KBr) 3040, 2928, 2900, 1660 (C=O), 1615, 1600 cm^{-1}; UV λ_{max} (methanol) 260 nm (ϵ 16 300); NMR ($CDCl_3$) δ 1.15 (8 H, m, CH_2 protons), 3.15 (2 H, m, bridgehead protons), 7.20 (10 H, m, aromatic protons); mass spectrum, *m*/*e* (relative intensity) 316 (M^+, 48), 288 (10), 260 (7), 248 (40), 238 (7), 211 (20), 209 (16), 183 (11), 165 (7), 155 (12), 141 (7), 128 (7), 105 (78), 77 (100), 51 (30).

Anal. Calcd for $C_{22}H_{20}O_2$: C, 83.03; H, 6.91. Found: C, 83.71; H, 5.99.

7-Oxa-2,3-dibenzoylbicyclo[2.2.1]hept-2-ene (16). A solution of 3.02 g (0.01 mol) of 7-oxa-2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**15**) in 150 mL of ethyl acetate was hydrogenated over 5% Pd on $CaCO_3$ at room temperature and 10 psi of H_2. After the reaction had been allowed to proceed for 15 min, the catalyst was removed by filtration, and the solvent was removed under reduced pressure. The residual solid was recrystallized from methanol to give 2.8 g (90%) of **16**: mp 92 °C; IR (KBr) ν_{max} 3040, 2950, 1660 (C=O), 1600 cm^{-1}; UV (methanol) λ_{max} 260 nm (ϵ 11 800); NMR ($CDCl_3$) δ 1.70–2.00 (4 H, m, CH_2 protons), 3.35 (2 H, m, bridgehead protons), 7.30 (10 H, m, aromatic protons); mass spectrum, *m*/*e* (relative intensity) 304 (M^+, 5), 277 (4), 276 (19), 275 (5), 248 (5), 247 (6), 230 (3), 220 (8), 219 (3), 200 (5), 199 (30), 143 (5), 115 (8), 105 (55), 77 (100), 51 (57).

Anal. Calcd for $C_{20}H_{16}O_3$: C, 65.79; H, 5.26. Found: C, 65.50; H, 5.32.

2,3-Dibenzoylbicyclo[2.2.1]hept-2-ene (19). A solution of 3.0 g (0.01 mol) of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene (**18**) was hydrogenated over 5% Pd on $CaCO_3$ in ethyl acetate for 15 min at room temperature and 10 psi of H_2. Workup of the mixture as in the earlier cases gave 2.8 g (93%) of **19**: mp 135 °C (lit.[24] mp 132.5 °C); IR (KBr) ν_{max} 3040, 2970, 2900, 1650 (C=O), 1615 cm^{-1}; UV (methanol) λ_{max} 260 nm (ϵ 14 450); NMR ($CDCl_3$) δ 1.50 (4 H, m, CH_2 protons at C_5 and C_6 positions), 1.95 (2 H, m, CH_2 protons at C_7 position), 3.50 (2 H, m, bridgehead protons), and 7.30 (10 H, m, aromatic protons); mass spectrum, *m*/*e* (relative

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(20) J. E. Harriman, *J. Chem. Phys.*, **40**, 2827 (1964).

(21) D. Döhnert and J. Koutecky, *J. Am. Chem. Soc.*, **102**, 1789 (1980), and references therein.

(22) Closely associated with the diradical singlet state of **28** is a low-lying triplet state calculated here to be 111 kcal/mol lower in energy than the closed-shell singlet state of **25**. By way of comparison, the triplet states of structures **24e**, **26**, and **23** were calulated to be 20, 76, and 78 kcal/mol higher in energy than the respective closed-shell singlet states.

(23) As for **28**, the RHF wave function of **24e** was also unstable in that a "singlet" UHF calculation gave a lower energy. But in contrast to **28**, the pure singlet component of the UHF wave function of **24e** was primarily of closed shell rather than diradical nature. This was evidenced by the charge-density natural-orbital occupation numbers[20] which were all close to 2 for the first 22 orbitals (1.90–2.00) with the remainder all being near 0 (0.00–0.10).

(24) G. Dupont and J. Germain, *C. R. Hebd. Seances Acad. Sci.*, **223**, 743 (1946); *Chem. Abstr.*, **41**, 2420 (1947).

(25) R. Adams and M. H. Gold, *J. Am. Chem. Soc.*, **62**, 56 (1940).

intensity) 302 (M$^+$, 25), 274 (11), 261 (5), 246 (2), 195 (5), 181 (8), 169 (4), 153 (3), 141 (5), 115 (5), 105 (100), 77 (98), 62 (8), 51 (5).

Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.45; H, 5.96. Found: C, 83.20; H, 6.15.

Thermolysis of 2,3-Dibenzoylbicyclo[2.2.2]oct-2-ene (12). A sample of 12 (1.0 g, 2.3 mmol) was heated in a sealed tube at around 310–320 °C for 1 h. The reaction mixture, after cooling, was chromatographed over silica gel. Elution with a mixture (4:1) of petroleum ether and benzene gave 400 mg (44%) of 2-benzoyl-3-phenylbicyclo[2.2.2]oct-2-ene (**14**): mp 124 °C (after recrystallization from petroleum ether); IR (KBr) ν_{max} 3040, 2900, 1641 (C=O), 1620, and 1600 cm^{-1}; UV (methanol) λ_{max} 230 nm (ϵ 8050), 247 (12 900), 254 (11 200), 282 (4700); NMR (CDCl$_3$) δ 1.68 (8 H, m, CH$_2$ protons), 3.45 (2 H, m, bridgehead protons), 7.00–7.50 (10 H, m, aromatic protons); mass spectrum, *m/e* (relative intensity) 288 (M$^+$, 84), 260 (13), 232 (3), 211 (8), 183 (7), 165 (5), 155 (18), 153 (14), 151 (11), 141 (8), 128 (11), 115 (15), 105 (80), 77 (100), 51 (15).

Anal. Calcd for $C_{21}H_{20}O$: C, 87.50; H, 6.90. Found: C, 87.32; H, 6.60.

Thermolysis of 2,3-Dibenzoyl-7-oxabicyclo[2.2.1]hept-2-ene (16). A sample of 16 (1.52 g, 5 mmol) was heated at around 310 °C for 1 h in a sealed tube. Workup of the mixture by chromatography over silica gel with elution with a mixture (4:1) of petroleum ether and benzene gave 1.02 g (74%) of 3,4-dibenzoylfuran (**17**): mp 131 °C; IR (KBr) ν_{max} 3180, 2956, 1660 (C=O), 1460, and 1300 cm^{-1}; UV (ethanol) λ_{max} 252 nm (ϵ 59 900); NMR (CDCl$_3$) δ 6.84 (6 H, m, phenyl protons), 7.19–7.25 (6 H, m, phenyl protons and the olefinic protons of the furan ring); mass spectrum, *m/e* (relative intensity) 276 (M$^+$, 26), 275 (6), 248 (4), 247 (4), 231 (2), 220 (8), 219 (6), 200 (8), 199 (52), 171 (40), 143 (5), 115 (20), 105 (60), 78 (12), 77 (100), 76 (5), 65 (5), 51 (40).

Anal. Calcd for $C_{18}H_{12}O_3$: C, 78.48; H, 4.30. Found: C, 78.74; H, 4.18.

Thermolysis of 2,3-Dibenzoylbicyclo[2.2.1]hept-2-ene (19). Heating of a sample of **19** (0.6 g, 2 mmol) at around 310 °C for 1 h and workup of the mixture by chromatography over silica gel with elution with a mixture (4:1) of petroleum ether and benzene gave 160 mg (30%) of 2-*endo*-3-*exo*-dibenzoylbicyclo[2.2.1]heptane (**20**): mp 106 °C; IR (KBr) ν_{max} 3080, 2940, 2870, 1665 (C=O), 1595, 1580 cm^{-1}; UV (ethanol) λ_{max} 210 nm (ϵ 5700), 248 (24 500), 278 (4150); NMR (CDCl$_3$) δ 1.43–1.83 (6 H, m, CH$_2$ protons), 2.67–2.88 (2 H, m, bridgehead protons), 4.27 (1 H, d, H$_3$ proton, $J_{2,3}$ = 4.0 Hz), 4.58 (1 H, m, H$_2$ proton), 7.63–8.13 (10 H, aromatic protons); mass spectrum, *m/e* (relative intensity) 304 (M$^+$, 3), 238 (20), 200 (6), 199 (43), 184 (3), 171 (14), 157 (2), 134 (3), 133 (33), 115 (2), 106 (8), 105 (100), 91 (3), 78 (6), 77 (63), 67 (3), 66 (11), 55 (9), 51 (5).

Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.88; H, 6.57. Found: C, 82.94; H, 6.47.

Hydrogenation of 2-*endo*-3-*exo*-Dibenzoylbicyclo[2.2.1]hept-5-ene (21). A solution of 1.56 g (5 mmol) of **21** in 150 mL of acetone was hydrogenated over 5% Pd on CaCO$_3$ for 1 h at room temperature and 10 psi of H$_2$. Removal of the catalyst by filtration and of the solvent under reduced pressure gave a product which on recrystallization from methanol gave 1.42 g (93%) of 2-*endo*-3-*exo*-dibenzoylbicyclo[2.2.1]heptane (**20**), mp and mmp 105–106 °C.

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Reactions of Cyclopropyl Chlorides with Metals and Lithium Naphthalene Radical Anion and Dianion[1]

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The reaction of *exo*- and *endo*-*anti*-3-chlorotricyclo[3.2.1.0^{2,4}]oct-6-ene with magnesium in THF followed by deuterolysis gave syn/anti deuteration ratios of 2.2 and 0.42, respectively, with 85% monodeuterium incorporation. Analysis of the exo hydrocarbon involved epoxidation followed by a shift-reagent study with Eu(fod)$_3$. Reaction of the same halides with Na/*t*-BuOD gave 95% deuterium incorporation with syn/anti ratios of 1.2 and 0.37, respectively. Similarly, reaction of *anti*-3-chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane with Na, K, and Li in *t*-BuOD/THF gave 95% deuterium incorporations with syn/anti ratios of 2.11, 1.25, and 1.70. No effect of temperature or solvent composition was observed in the potassium reduction. Reaction of this halide with Li in Et$_2$O followed by D$_2$O gave 87% deuterium incorporation with a syn/anti ratio of 2.1, while reaction with lithium naphthalene in THF at −78 °C followed by addition of D$_2$O gave 96% deuterium incorporation with a *syn*/anti ratio >100. All of the above results are described in terms of radical equilibria and competing electron transfers. Reaction of *anti*-3-bromo-*exo*-tricyclo[3.2.1.0^{2,4}]octane with butyllithium in ether at 0 °C followed by deuterolysis gave entirely anti deuteration (anti/syn ratio >16) with 95% deuterium incorporation. Reaction of *anti*-3-chloro-*exo*-tricyclo[3.2.1.0^{2,4}]octane with lithium naphthalene dianion proceeded at −78 °C in THF with a rate constant of 5.5 × 10^{-2} M^{-1} min^{-1}, while under identical conditions lithium naphthalene exhibited a rate constant of 1.0 M^{-1} min^{-1}. Deuterolysis of the dianion solution gave a *syn* to *anti* deuterium incorporation ratio greater than 50.

Our original interest in the reactions of metals and alkali radical anions with cyclopropyl chlorides was sparked by the need to develop methods for replacement of a leaving group at C-3 in tricyclo[3.2.1.0^{2,4}]oct-6-ene (1) or tricyclo[3.2.1.0^{2,4}]octane (**5**) systems with deuterium in a stereospecific manner, so that either syn (**2**, **6**) or anti (**3**, **7**) 3-deuterio substrates could be prepared. During the course of our study, procedures for the desired transformations were successfully developed, and the very interesting intrinsic nature of these transformations emerged as the dominant theme of our investigation.

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[1] Reported in part in preliminary form: P. K. Freeman, L. L. Hutchinson, and J. N. Blazevich, *J. Org. Chem.*, **39**, 3606 (1974).

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