Epimerization of Optically Pure (−)-(*Z*)-1 in Methanol and in Benzene (Runs 14–17). Run 14. Optically pure (−)-(*Z*)-**1** (0.300 g) in 3 ml of purified methanol was heated in a degassed, sealed ampoule at 185° for 200 min (10% epimerization). The product mixture was chromatographed on 90 g of silica gel (1.9 × 67 cm column) using 5% ether–pentane mixture as eluent and taking 10-ml fractions. Fractions 53–63 were pure (*Z*)-**1** by glc. The materials from these fractions were combined and after distillation had $[\alpha]^{25}_{546}$ −272° (*c* 0.28, $CHCl_3$). Fractions 70–79 were all >50% (*E*)-**1** in composition. These fractions were combined and after distillation had the observed rotation: α^{25}_{546} −0.308° (4.977 mg in 1.00 ml of $CHCl_3$). The composition of the rotation sample was determined by glc to be 34.1% (*Z*)-**1** and 65.9% (*E*)-**1**. The contribution of (−)-(*Z*)-**1** to the observed rotation was calculated to be −0.462°, and the contribution of (+)-(*E*)-**1** to be (+)-0.154°. From these values, the (+)-(*E*)-**1** produced from (−)-(*Z*)-**1** was calculated to be $[\alpha]^{25}_{546}$ +47.0° (*c* 0.328, $CHCl_3$). Internally consistent rotations were obtained at λ 436 and 365 nm. Control experiments are recorded in the following section, and Table III records the results.

Run 15. Optically pure (−)-(*Z*)-**1** (0.113 g) in 2 ml of methanol was heated (see Table III), and the product was glc analyzed and isolated by chromatography (43 g of silica gel). Fractions 29–31 gave pure (*Z*)-**1** (glc), $[\alpha]^{25}_{546}$ −270° (*c* 0.304, $CHCl_3$), and fractions 46–55 were collectively 25.1% (*Z*)-**1** and 74.9% (*E*)-**1**, and gave the observed rotation: α^{25}_{546} −0.094° (2.900 mg in 1.00 ml of $CHCl_3$). The contribution of (−)-(*Z*)-**1** to the observed rotation was calculated to be −0.197°, and that of (+)-(*E*)-**1** to be 0.103°. The rotation of the (+)-(*E*)-**1** produced was calculated to be $[\alpha]^{25}_{546}$ +47.4° (*c* 0.217, $CHCl_3$). Internally consistent results were obtained at λ 436 and 365 nm. Table III records the results.

Run 16. Optically pure (−)-(*Z*)-**1** (0.100 g) in 1 ml of methanol was heated (Table III), and the product was glc analyzed and isolated by chromatography (40 g of silica gel). Fractions 27–32 gave pure (*Z*)-**1** having $[\alpha]^{25}_{546}$ −268.4° (*c* 0.166, $CHCl_3$). Fractions 45–55 were combined. By glc the composite was 17.2% (*Z*)-**1** and 82.2% (*E*)-**1**. The observed rotation was α^{25}_{546} +0.024° (3.060 mg in 1.00 ml of $CHCl_3$). The contribution of (−)-(*Z*)-**1** to the observed rotation was calculated to be −0.141°, and that of (+)-(*E*)-**1** to be +0.117°. The calculated rotation of the (+)-(*E*)-**1** produced was $[\alpha]^{25}_{546}$ +46.2° (*c* 0.253, $CHCl_3$). Internally consistent rotations were obtained at λ 436 and 365 nm. Table III records the results.

Run 17. Optically pure (−)-(*Z*)-**1** (0.164 g) in 2 ml of benzene was treated as indicated in Table III, and the product was glc analyzed and isolated by chromatography (50 g of silica gel). Fractions 24–27 gave pure (glc) (*Z*)-**1**, $[\alpha]^{25}_{546}$ −270° (*c* 0.122, $CHCl_3$). Fractions 39–46 were combined, and the composite was (glc) 15.6% (*Z*)-**1** and 84.4% (*E*)-**1**. Its observed rotation was α^{25}_{546} −0.006° (3.598 mg in 1.00 ml of $CHCl_3$). The contribution (−)-(*Z*)-**1** to the observed rotation was calculated to be −0.151°, and of (+)-(*E*)-**1** to be +0.145°. The rotation of the (+)-(*E*)-**1** produced in the epimerization was calculated to be $[\alpha]^{25}_{546}$ +47.7° (*c* 0.304, $CHCl_3$). Internally consistent rotations were obtained at λ 436 and 365 nm. Table III records the results.

Control Experiments. A sample of (−)-(*Z*)-**1** of $[\alpha]^{25}_{546}$ − 126° was distilled exhaustively onto a Dry Ice cooled cold finger at 90° at 5 μ to give (−)-(*Z*)-**1** of $[\alpha]^{25}_{546}$ −124°. This material was distilled a second time to give $[\alpha]^{25}_{546}$ −127°. Thus (−)-(*Z*)-**1** was optically stable to distillation.

A sample of (−)-(*E*)-**1** of $[\alpha]^{25}_{546}$ −43.1° was subjected to two exhaustive distillations (see above) to give $[\alpha]^{25}_{546}$ −43.1° and $[\alpha]^{25}_{546}$ −43.2° after the first and second distillations, respectively. Thus (−)-(*E*)-**1** was optically stable to distillation.

The additivity of the rotations of (−)-(*Z*)-**1** and (+)-(*E*)-**1** was demonstrated as follows. Optically pure (−)-(*Z*)-**1** (1.165 mg) and (+)-(*E*)-**1** (3.395 mg) were dissolved in 2.00 ml of chloroform, and the solution gave observed rotations of α^{25}_{546} −0.066° and α^{25}_{436} −0.083°. The rotations of the mixture calculated from the amounts of each and their specific rotations were α^{25}_{546} −0.065° and α^{25}_{436} −0.081°. The observed and calculated are within experimental error of one another.

About 240 mg of (−)-(*Z*)-**1**, $[\alpha]^{25}_{546}$ −256° (94% optically pure), was chromatographed on 70 g of silica gel using 5% ether–pentane mixture as eluent. Product was eluted in fractions 36–45. The specific rotations of the (−)-(*Z*)-**1** in fractions 37, 40, 43 and 45 were determined after the material was exhaustively distilled and were all $[\alpha]^{25}_{546}$ −258°, or of 95% optical purity.

About 60 mg of (−)-(*E*)-**1**, $[\alpha]^{25}_{546}$ −44° (79% optically pure), was chromatographed on 70 g of silica gel. The product was eluted in fractions 44–52. The specific rotations of the (−)-(*E*)-**1** in selected fractions were determined after each sample was exhaustively distilled, and were as follows: fraction 45, $[\alpha]^{25}_{546}$ −44.6° (80.5% optically pure); fraction 49, $[\alpha]^{25}_{546}$ −44.8° (80.5% optically pure); fraction 52, $[\alpha]^{25}_{546}$ −43 ± 2° (77.5 ± 3.5% optically pure). So little material was available in fraction 52 that the limits of error were much larger than for the other fractions. These results indicate that no optical fractionation or racemization of (−)-(*Z*)-**1** or (−)-(*E*)-**1** occurs during chromatography.

Stereospecificity of "Retro-Diels–Alder" Fragmentation under Electron Impact

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Contribution from the Department of Chemistry, Israel Institute of Technology, Haifa, Israel. *Received October 30, 1972*

Abstract: "Retro-Diels–Alder" fragmentation under electron impact and two analogous processes which are accompanied by hydrogen migrations are highly stereospecific in three systems of diketones. The resulting ions a, b, and c are very abundant in the case of cis isomers **3**, **7**, and **9**, but of negligible abundance in trans diketones **4**, **8**, and **10**. The high degree of stereospecificity suggests that no rearrangement of the molecular ions to common structures precedes these fragmentation processes, and that two C,C bonds are cleaved concurrently in the course of retro-Diels–Alder fragmentation and the analogous processes in the examined systems.

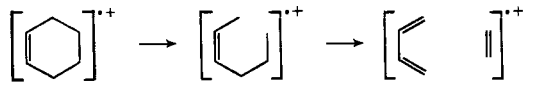
The electron-impact-induced "retro-Diels–Alder" fragmentation is one of the most important processes occurring in many organic compounds which contain a double bond in a six-membered ring.[3,4] This process provides a unique method for structure determination in polycyclic compounds of consider-

(1) Based in part on the M.Sc. Thesis of A. Karpati, 1969.
(2) Based in part on the D.Sc. Thesis of J. Deutsch, 1971.
(3) H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, 21, 1855 (1965).
(4) (a) K. Biemann, "Mass Spectrometry," McGraw-Hill, New York, N. Y., 1962, pp 102–107; (b) H. Budzikiewicz, D. H. Williams, and C. Djerassi, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 67–71; (c) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1966, p 118; (d) S. E. Drewes and H. Budzikiewicz, *J. Chem. Soc. C*, 63 (1969); (e) C. Wünsche and J. Löw, *Tetrahedron*, 22, 1893 (1966).

able complexity, like many terpenoids, steroids, and other natural products, where other physical methods do not give unambiguous solutions.[5]

Two suggestions have been made for the possible mechanism of the retro-Diels–Alder fragmentation. The stepwise process shown in Scheme I is favored by

Scheme I

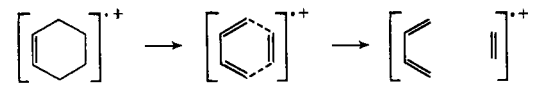


A

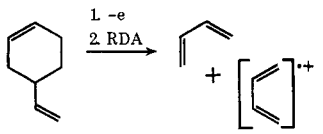
Budzikiewicz, Brauman, and Djerassi,[3] based on the charge distribution between the fragmentation products and on energy considerations. The abundances of the two possible ions (butadiene and ethylene) correspond well with the predicted charge distribution in the open-chain intermediate A.

The concerted mechanism shown in Scheme *II* is

Scheme II



favored by Dougherty on theoretical grounds.[6] This mechanism resembles the thermal electrocyclic RDA fragmentation, and it is supported by the experimental results of Smith and Thornton, who found that after decomposition of 4-vinylcyclohexene under electron impact, charge is preferentially retained in the butadiene ion which contains the vinyl group rather than in the other butadiene originating from the ring.[7]

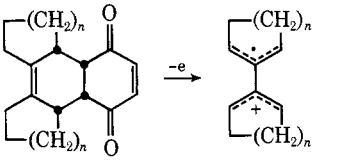


Elwood and Beynon[8] suggest that a correlation exists between the kinetic energy released in the metastable transitions of the RDA reaction of several gaseous bicyclic hydrocarbon ions and the ground-state activation energies for the Diels–Alder formation of similar neutral species in solution. This finding seems to support again the concerted mechanism.

As a stereochemical approach to the question of the mechanism of retro-Diels–Alder fragmentation, we have investigated the mass spectra of some stereoisomers, in which the double bond of the resulting neutral olefin fragment is part of a six-membered ring. If the electron-impact-induced retro-Diels–Alder fragmentation occurs *via* a concerted mechanism, and further if it follows the steric requirements of the thermally allowed process,[9] only stereoisomers giving rise to cis olefins should be reactive. This conclusion can of course be valid only if the molecular ions do not rearrange before fragmentation takes place.

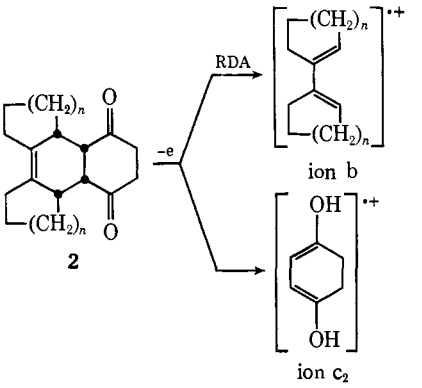
Results and Discussion

In previous publications, we discussed the RDA fragmentation under electron impact in the tetra- and pentacyclic diketones **1**, **2**, and **3**.[10,11] Adducts (**1**) of *p*-



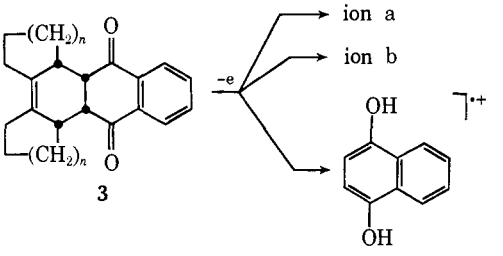
1 ion a

benzoquinone and bicycloalkenyls do not undergo an appreciable RDA fragmentation. A site-specific double hydrogen migration occurs in these adducts ($n < 3$[12]), and the abundant ions (proposed structure a) are lighter by 2 mass units than the expected RDA fragments.[10] In the reduced diketones (**2**), two related



2 ion b ion c_2

fragmentation processes were detected: (a) regular RDA fragmentation with the retention of the positive charge in the diene (ion b); (b) double hydrogen migration accompanying a process similar to RDA, leading to ion c_2.[11] In the adducts of naphthoquinone **3** the



3 ion c_3 (*m/e* 160)

three processes were detected, and the corresponding ions a, b, and c_3 were of relatively high abundance.[11]

The reduced system **2** was the simplest for a study of the effect of configuration on RDA fragmentation. The trans diketones **4** were easily formed by a short

(5) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. 1 and 2, Holden-Day, San Francisco, Calif., 1964; see Index (Retro-Diels–Alder decomposition); A. K. Barua, P. Chakrabarti, S. P. Dutta, and D. K. Mukherjee, *Tetrahedron*, 27, 1141 (1971); U. Claussen, H.-W. Fehlhaber, and F. Korte, *ibid.*, 22, 3535 (1966); G. Berti, F. Bottari, A. Marsili, I. Morelli, and A. Mandelbaum, *Chem. Commun.*, 50 (1967); *Tetrahedron Lett.*, 529 (1968); G. Berti, A. Marsili, I. Morelli, and A. Mandelbaum, *Tetrahedron*, 27, 2217 (1971); W. Wiegrebe, L. Faber, H. Brockmann, H. Budzikiewicz, and U. Krueger, *Justus Liebigs Ann. Chem.*, 721, 154 (1969); C. K. Yu, D. B. MacLean, R. G. A. Rodrigo, and R. H. F. Manske, *Can. J. Chem.*, **48**, 3673 (1970), and many others.

(6) R. C. Dougherty, *J. Amer. Chem. Soc.*, 90, 5788 (1968).

(7) E. P. Smith and E. R. Thornton, *J. Amer. Chem. Soc.*, **89**, 5079 (1967).

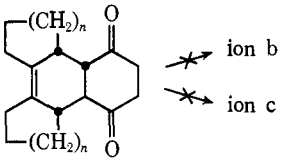
(8) Th. A. Elwood and J. H. Beynon, 19th Annual Conference on Mass Spectrometry and Allied Topics, Atlanta, Ga., May 1971, p 173.

(9) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

(10) J. Deutsch and A. Mandelbaum, *J. Amer. Chem. Soc.*, **91**, 4809 (1969).

(11) J. Deutsch and A. Mandelbaum, *Org. Mass Spectrom.*, **5**, 53 (1971).

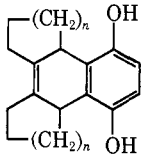
(12) J. Deutsch and A. Mandelbaum, *J. Chem. Soc. B*, 886 (1971).



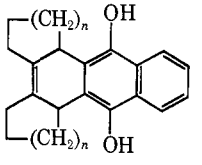
4

treatment of the cis analogs **2** with sodium methoxide in methanol. The mass spectra of isomers **2** and **4**[13] show that both the regular RDA fragmentation and the 2H-migration-accompanied RDA process do not operate in the trans isomers, and ions b and c_2, which are abundant in the cis isomers **2**, are practically absent in the trans diketones **4**.

A similar examination of the stereospecificity of RDA fragmentation (and its analogs which are accompanied by hydrogen migrations) was not possible in systems **1** and **3**, because under the conditions of epimerization they undergo isomerization to the stable tautomers, *i.e.*, substituted hydroquinones **5** and **6**. In order to

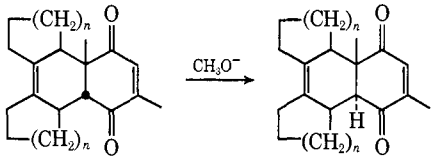


5



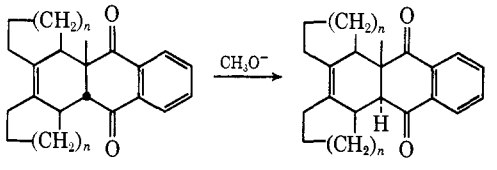
6

overcome this difficulty the analogous diketones **7** and **9** were synthesized, and were readily converted to the trans isomers **8** and **10** by treatment with sodium methoxide.



7a, $n = 1$
b, $n = 2$
c, $n = 3$

8



9a, $n = 1$
b, $n = 2$
c, $n = 3$

10

As often happens, here too the introduction of a small structural change led to pronounced differences in the fragmentation under electron impact. The introduction of the additional methyl groups in the angular positions in **7** and **9** enhances the regular RDA fragmentation leading to the diene ion b. Therefore both ions a and b are abundant in the mass spectra of adducts **7**, in contrast to **1**, and ion a is practically absent from the mass spectra of **9** (in contrast to **3**).

(13) The mass spectra will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-73-4244. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

The mass spectra of pairs of isomers **7** and **8** and of **9** and **10** are entirely different.[13] RDA fragments (ions b) as well as the hydrogen-migration-accompanied analogs (ions a) are of very high abundance in the case of cis diketones **7** (they give rise to the most intense peaks in the mass spectra of **7a** and **7b**). RDA fragmentation affords the most abundant ion b in the mass spectra of cis diketones **9**, and rearrangement ion c is also of relatively high abundance. Ions a, b, and c are of very low abundance or practically absent in the trans isomers **8** and **10**. The relative abundances of ions a and b are listed in Table I.

Table I. Abundances of Ions a and b in the Isomeric Diketones

	Ion b, cis			Ion b, trans		
m/e	Compd	b/M$^+$	% Σ_{40}	Compd	b/M$^+$	% Σ_{40}
134	**7a**	1.9	13.7	**8a**	0.1	1.1
162	**7b**	1.3	8.5	**8b**	0.02	0.3
190	**7c**	3.7	4.4	**8c**	0.04	0.4
134	**9a**	4.5	32.5	**10a**	0.4	4.5
162	**9b**	4.6	24.3	**10b**	0.01	0.2
190	**9c**	5.7	27.0	**10c**	<0.01	0.16
	Ion a, cis			Ion a, trans		
m/e	Compd	a/M$^+$	% Σ_{40}	Compd	a/M$^+$	% Σ_{40}
132	**7a**	2.85	20.4	**8a**	0.08	0.9
160	**7b**	2.0	12.8	**8b**	0.04	0.7
188	**7c**	1.2	1.4	**8c**	0.06	0.5
132	**9a**	0.05	2.7	**10a**	0.04	0.6
160	**9b**	0.5	2.6	**10b**	0.02	0.3
188	**9c**	0.07	0.35	**10c**	<0.01	0.1

The molecular ions are the most abundant species in the case of all the trans isomers **8** and **10**, in contrast to cis diketones **7** and **9**. The sums of abundances of all ions that are lighter than ion a are smaller in the mass spectra of all trans diketones **8** and **10** than in the cis isomers (see Table II). These findings exclude the

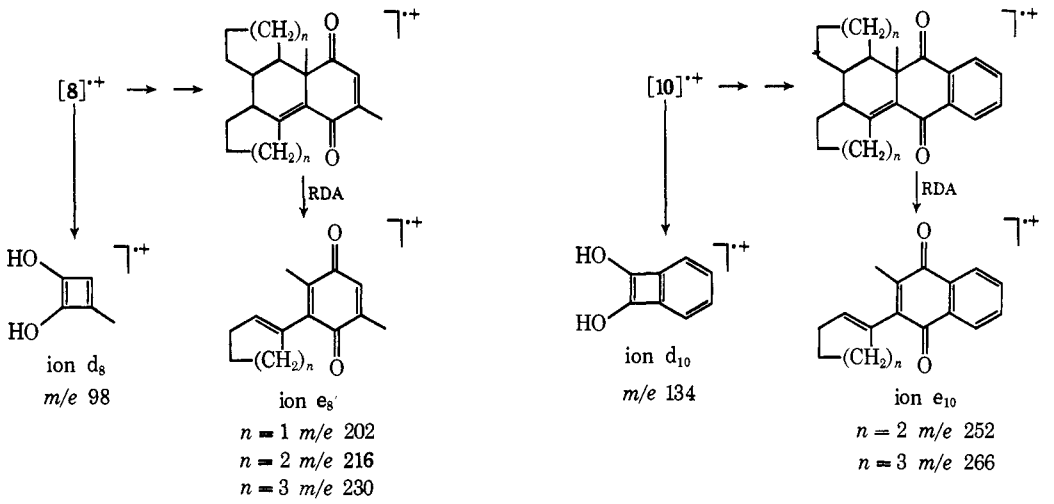
Table II. Sums of Abundances of Ions from *m/e* 40 to Ion a

Cis		Trans	
Compd	Σ(% Σ_{40})	Compd	Σ(% Σ_{40})
7a	41	**8a**	34
7b	43	**8b**	38
7c	89	**8c**	63
9a	34	**10a**	33
9b	52	**10b**	40
9c	58	**10c**	50

possibility of explaining the absence (or low abundance) of ions a, b, and c in trans isomers **8** and **10** as resulting from enhanced decomposition of these ions in these particular isomers. It must therefore be concluded that RDA fragmentation (leading to ion b) and its hydrogen-migration-accompanied analogs occur specifically in the cis isomers **7** and **9** but do not occur practically in the trans isomers **8** and **10**.

The trans diketones **8** and **10**, which cannot undergo RDA fragmentation, find other pathways of decomposition. Enhanced loss of a methyl radical is one such pathway. [M − CH_3]$^+$ ions are of higher abundance in the trans isomers than in those having cis fusion of rings A and B. Another general process

Scheme III



which is specific to the trans isomers yields ions d_8 of *m/e* 98 and d_{10} of *m/e* 134 in diketones **8** and **10**, respectively. The fact that the *m/e* values of these ions change with the variation of the quinone part of the molecule, but are independent of the size of rings C and D in **8** and D and E in **10**, indicates that these ions are composed of the elements of ring A in **8** and rings A and B in **10**. Possible structural representation is given in Scheme III.

Another stereospecific fragmentation characteristic of the trans isomers is that leading to the prominent peaks at *m/e* 202, 216, 230, 252, and 266 in the mass spectra of **8a**, **8b**, **8c**, **10b**, and **10c**, respectively. It is evident from the *m/e* values of these ions e that they contain only one of the two rings C and D in **8**, and D and E in **10**. The difference between the molecular weights and the *m/e* values of these ions corresponds to the loss of a cycloalkene molecule having the size of one of rings C, D, or E from the molecular ion. A possible mechanism involving double bond migration and RDA fragmentation is suggested in Scheme III. All the fragmentations in the trans isomers **8** and **10** are relatively slow, resulting in the high abundance of the molecular ions, which give rise to the most intense peaks in the mass spectra.

It should be emphasized that any conclusions drawn from the results described above are limited to the systems used in this study. In these systems practically no rearrangement leading to a common structure occurs in the molecular ions prior to the RDA fragmentation. The fact that in all cases cis isomers undergo relatively fast RDA fragmentation, while the trans isomers do not, strongly suggests that this fragmentation does not occur in these systems as a two-step process. This supports Dougherty's[6] and Thornton's[7] work. Equally noteworthy, the fact that only cis isomers react suggests that the electron-impact-induced RDA process follows selection rules predicted for a thermal reaction[14] rather than for a photochemical analog.[15]

It is also apparent from the results of this work that high stereoselectivity of electron-impact-induced processes is not necessarily connected with hydrogen migration.[16] A defined mechanistic pathway which may be easily accessible for one isomer but unfavored for the other may result in extreme differences in mass spectral behavior, if, of course, rearrangements to common structures do not occur, or are relatively slow.

Experimental Section

Melting points (mp) are uncorrected. Mass spectra were measured with an Atlas CH4 mass spectrometer fitted with a TO-4 ion source and direct inlet system, operated without heating. The samples were heated externally, if necessary, until the ion current was sufficient to provide usable mass spectra. The ionization energy was maintained at 70 eV.

Preparation of Adducts 7 and 9. A solution of quinone (2,4-dimethylbenzoquinone for **7**, and 2-methylnaphthoquinone for **9**) and diene (10% excess, bi-1-cyclopenten-1-yl for **7a**, and **9a**, bi-1-cyclohexen-1-yl for **7b** and **9b**, and bi-1-cyclohepten-1-yl for **7c** and **9c**) in ethanol, benzene, or toluene was refluxed for 12–48 hr. The formation of the adduct was followed by thin layer chromatography. The solvent was evaporated off, and the pure product was obtained by two recrystallizations from methanol or ethanol. In all cases ir, nmr, and mass spectra confirmed the structures.

7a: mp 76–77° (methanol). *Anal.* Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20; O, 11.84. Found: C, 79.67; H, 8.08; O, 12.09; mol wt 270 (mass spectrum).

7b: mp 137–138° (ethanol). *Anal.* Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78. Found: C, 80.29; H. 8.51; mol wt 298 (mass spectrometry).

7c: mp 111–113° (ethanol). *Anal.* Calcd for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26. Found: C, 81.30; H, 9.36; mol wt 326 (mass spectrometry).

9a: mp 92–93° (methanol). *Anal.* Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.63; H, 7.26; mol wt 306 (mass spectrometry).

9b: mp 179–180° (methanol–methylene chloride). *Anal.* Calcd for $C_{23}H_{26}O_2$: C, 82.59; H, 7.84. Found: C, 82.00; H, 7.78; mol wt 334 (mass spectrometry).

9c: mp 113–117° (ether). *Anal.* Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.49; H, 8.30; mol wt 362 (mass spectrometry).

Preparation of Trans Diketones. The corresponding cis diketones **2**, **7**, and **9** were epimerized by heating under reflux in a solution of sodium methoxide (0.1 *N*) in absolute methanol in an inert atmosphere for 1–4 hr. After the solution was cooled, the solution was

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acidified by 10% HCl. Recrystallization of the precipitate yielded pure product. In one case (**8c**) the product was an oil. **8b** (mp 81°) was isolated by preparative thin layer chromatography, and identified by its ir, nmr, and mass spectra.

8a: mp 105–106° (methanol). *Anal.* Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.48; H, 8.17; mol wt 270 (mass spectrometry).

10a: mp 141–142° (hexane). *Anal.* Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.76; H, 7.16; mol wt 306 (mass spectrometry).

10b: mp 145° (ethanol). *Anal.* Calcd for $C_{23}H_{26}O_2$: C, 82.59; H, 7.84. Found: C, 82.32; H, 7.68; mol wt 334 (mass spectrometry).

10c: mp 127–128° (ethanol). *Anal.* Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.49; H, 8.30; mol wt 362 (mass spectrometry).

Acidity of Hydrocarbons. XLVI. Equilibrium Ion-Pair Acidities of Mono-, Di-, and Triarylmethanes toward Cesium Cyclohexylamide[1]

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Abstract: Equilibrium ion-pair acidities relative to 9-phenylfluorene (PF) are reported for 16 hydrocarbons toward cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA). The effects of phenyl and methyl substituents and of cyclic structures on relative pK's illustrate the relative importance of conjugation and inductive effects, rotational entropy and steric effects, and conformational interactions. For the pK of PF taken as 18.49, the following pK values are obtained: *p*-methylbiphenyl (pMB), 38.7; bis(2,4-dimethylphenyl)methane (DXM, "dixylylmethane"), 36.3; di-*p*-tolylmethane (DpTM), 35.1; di-*o*-tolylmethane (DoTM), 34.8; 5-methyl-5*H*-dibenzo[*a*,*d*]cyclohepta-1,3-diene (MDCH), 33.6; diphenylmethane (DPM), 33.4; tri-*p*-tolylmethane (TpTM), 33.0; 5-phenyl-5*H*-dibenzo[*a*,*d*]cyclohepta-1,3-diene (PDCH), 31.6; triphenylmethane (TPM), 31.4; 5*H*-dibenzo[*a*,*d*]cyclohepta-1,3-diene (DCH), 31.2; bis-*p*-biphenylylmethane (BBM), 30.8; 9,9-dimethyl-9,10-dihydroanthracene (DDA), 30.3; 9,9,10-trimethyl-9,10-dihydroanthracene (TDA), 30.3; *p*-biphenylyldiphenylmethane (BDPM), 30.2; 10-phenyl-9,9-dimethyl-9,10-dihydroanthracene (PDDA), 28.0; 10-*p*-biphenylyl-9,9-dimethyl-9,10-dihydroanthracene (BDDA), 27.7.

In the construction of thermodynamic acidity scales for hydrocarbons, two important approaches have been the application of H_- techniques in various solvent systems[3] and emf techniques as in the use of the glass electrode in DMSO.[4] These approaches are generally successful down to acidities as low as pK's in the 20's where many fluorene derivatives lie; however, di- and triarylmethanes generally are of still lower acidity and are not measured accurately by these techniques. We have previously reported[5] a number of relative acidities based on competitive equilibria with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA).

$$RH + R'^-Cs^+ \rightleftharpoons R^-Cs^+ + R'H \qquad (1)$$

This method gives quantitative values for equilibrium *ion-pair acidities*, but for hydrocarbons with highly delocalized conjugate bases, such values compare well with the corresponding equilibrium *ionic acidities*, and, especially for closely related systems, serve quite well for assessing substituent and structural effects on carbanion stabilities. In the present paper, we extend this method to a number of di- and triarylmethanes and even to a monoarylmethane, *p*-methylbiphenyl (pMB). The results are used to explore a number of structural effects in carbanions including phenyl and methyl substituent effects, charge distributions, and the effects of rotational entropy.

Experimental Section

Hydrocarbons. Most of the hydrocarbons used in the present study have been reported previously together with spectral data of their cesium salts in CHA:[5-8] diphenylmethane (DPM), triphenylmethane (TPM), 1,1-diphenylethane (DPE), 10-phenyl-9,9-dimethyl-9,10-dihydroanthracene (PDDA), 9,9,10-trimethyl- (TDA) and 9,9-dimethyl-9,10-dihydroanthracene (DDA), 5-methyl- (MDCH) and 5-phenyl-5*H*-dibenzo[*a*,*d*]cycloheptadiene (PDCH) and the parent hydrocarbon (DCH), *p*-methylbiphenyl (pMB), di-*o*-tolylmethane (DoTM), di-*p*-tolylmethane (DpTM), bis(2,4-dimethylphenyl)methane (DXM), di-*p*-biphenylylmethane (DBM), and tri-*p*-tolylmethane (TpTM).

10-Biphenylyl-9,9-dimethyl-9,10-dihydroanthracene. This compound was prepared by a sequence starting with the reaction of *p*-biphenylylmagnesium bromide with 10,10-dimethylanthrone.[9] The formation of the *p*-biphenylylmagnesium bromide, reputedly

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