Ring Opening Reactions of Triphenylcyclopropyl Anions. II. An Apparent Disrotatory Opening of a Cyclopropyl Anion[1]

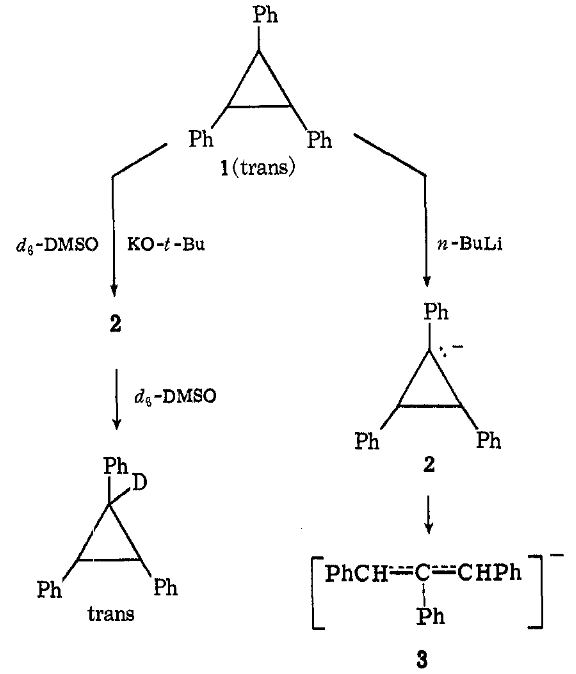
MICHAEL E. LONDRIGAN[2] AND J. E. MULVANEY*

Department of Chemistry, The University of Arizona, Tucson, Arizona 85721

Received February 16, 1972

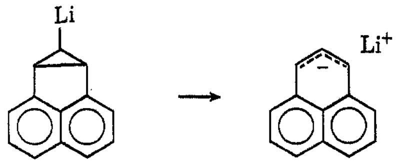
2,3,4-Triphenyl-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane (**6**) and 2,3,4-triphenyl-*endo*-tricyclo[3.2.1.$0^{2,4}$]-6-octene (**7**) rearrange to 2,3,4-triphenylbicyclo[3.2.1]-2-octene (**8a**) and 2,3,4-triphenyltricyclo[3.2.1.$0^{2',7'}$]-3-octene (**9**), respectively, upon treatment with potassium *tert*-butoxide in dimethyl sulfoxide. Although the reactions require the orbital symmetry forbidden disrotatory transformation of a cyclopropyl anion to an allylic anion, it is likely that the opening does not occur in a concerted manner. Evidence is presented that the conjugate base of **7** consists of one or more discrete ions rather than a delocalized bishomocyclopentadienyl anion.

In a preceding paper it was shown that *trans*-1,2,3-triphenylcyclopropane (**1**) undergoes ring opening upon treatment with organolithium compounds to give the 1,2,3-triphenylallyl carbanion (**3**). However, when **1** is treated with potassium *tert*-butoxide in d_6-dimethyl sulfoxide (d_6-DMSO), the cyclopropyl carbanion is intercepted by the solvent before the ring opening occurs.[3]



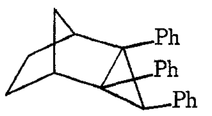
Because there are stereoisomers of **2** and because **3** undergoes rotational isomerization under the reaction conditions,[3] it was not possible to determine whether the conversion of the cyclopropyl anion **2** to the allylic ion **3** occurs by an orbital symmetry allowed conrotatory process or by the forbidden disrotatory opening.[4]

To our knowledge there are only three examples of the ring opening of a cyclopropyl anion or anionlike intermediate. Huisgen has observed the allowed thermal conrotatory-photochemical disrotatory opening of the isoelectronic aziridine to the azomethine ylide.[5] Boche, Martens, and Danzer have observed a conrotatory thermal opening of a cyclopropyl anion to a cyclononatetraenyl anion;[6] Wittig, Rautenstranch, and Wingler[7] observed the transformation **4** → **5**, an apparent disrotatory opening, but this reaction required a temperature of 100° for 24 hr, and the mechanism of the ring opening is not necessarily apparent and could invoke homolytic bond scission.[8]



4 **5**

To determine the stereochemistry of the opening of a triphenylcyclopropyl anion, 2,3,4-triphenyl-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane (**6**) and 2,3,4-triphenyl-*endo*-tricyclo[3.2.1.$0^{2,4}$]-6-octene (**7**) were treated with base.



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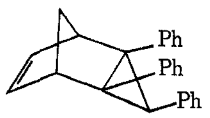

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Using potassium *tert*-butoxide in d_6-DMSO at room temperature, conditions under which both *cis*- and *trans*-1,2,3-triphenylcyclopropane exchanged cyclo-

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[1] Work supported by the National Science Foundation from The University of Arizona Science Development Program.

[2] Recipient of an NSF Traineeship, 1968–1972.

[3] J. E. Mulvaney and D. J. Savage, *J. Org. Chem.*, **36**, 2592 (1971).

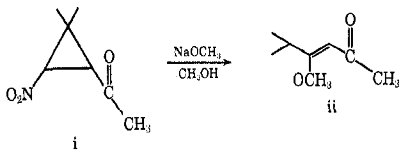
[4] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim, 1970.

[5] R. Huisgen, W. Scheer, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 1753 (1967).

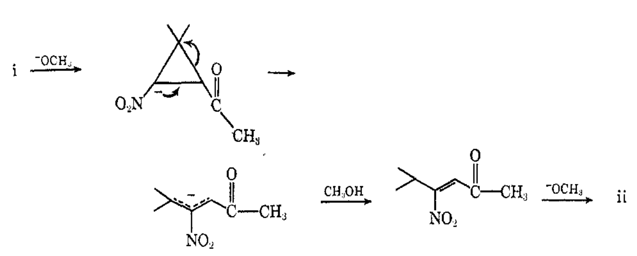
[6] G. Boche, D. Martens, and W. Danzer, *Angew Chem., Int. Ed. Engl.*, **8**, 984 (1969).

[7] G. Wittig, V. Rautenstranch, and F. Wingler, *Tetrahedron, Suppl. No. 7*, 189 (1966).

[8] Another reaction which may involve the opening of a cyclopropyl anion is the conversion of i to ii. Evidence was presented to indicate that

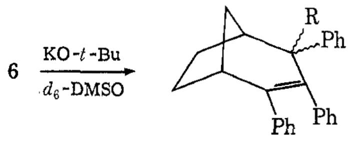


the mechanism was the following.[9]



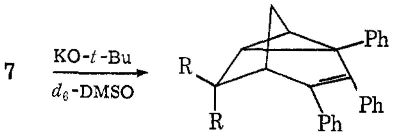
[9] L. I. Smith and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **71**, 2676 (1949).

propyl hydrogens, but did not undergo ring opening,[3] compounds **6** and **7** were recovered with no ring opening or hydrogen exchange. The lack of exchange may be due to a steric effect. However, at 70° after 20 hr both **6** and **7** were essentially completely converted to new compounds, **8** and **9**, respectively.



(1)

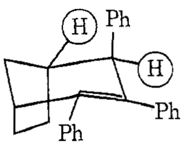
8a, R = H
b, R = D



(2)

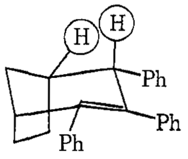
9a, R = H
b, R = D

Compound **8a**, mp 151–153° was isolated pure in 85% yield and had the expected composition. Although the highly hindered double bond does not react with Br_2–CCl_4 or $KMnO_4$ *cis*-stilbenyl unsaturation manifested itself in the uv spectrum $\epsilon_{258\ nm}$ 9680. The most significant aspect of the nmr spectrum of **8** is the lowest field signal at τ 6.25 (J = 2 Hz). This doublet must be due to the proton at C-4, and the low value of the coupling constant is consistent with equatorial–equatorial or equatorial–axial coupling[10] between the proton at C-4 and C-5 (see **8c** and **8d**). The product **8b** obtained when the **6** → **8** conversion was carried out in d_6-DMSO contained 0.98 D/molecule and the low field signal at τ 6.25 was absent.



8c

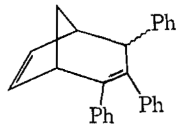
e–e coupling



8d

e–a coupling

The nmr of **9** obtained from reaction 2 (mp 157–158°, 75% isolated) shows no olefinic hydrogens in the τ 4–5 region. Just as in the case of **8** the highly hindered stilbenyl double bond of **9** does not react with permanganate, but in contrast a positive Br_2–CCl_4 test was obtained. We consider this a manifestation of the vinyl and phenyl conjugated cyclopropyl ring in **9**. These observations rule out the possibility of **10** as the product. Furthermore, the quadricyclane **11** was prepared[11] and comparison of physical and spectroscopic properties definitely rules this compound out as the product of reaction 2. Particularly noteworthy is the absence of a low field signal in **9** in the region τ 5.69 assigned to the benzylic proton at C-3 in **11**. The uv of compound **11** has $\epsilon_{275,224\ nm}$ 750, 21,000, whereas product **9** has $\epsilon_{277\ nm}$ 11,300. A high field multiplet at τ 8.1 in **9** is consistent with the cyclopropyl hydrogens.[12] When reaction 2 is carried out in d_6-DMSO, the product, **9b**, contains 1.50 D/molecule.



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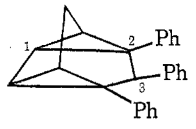

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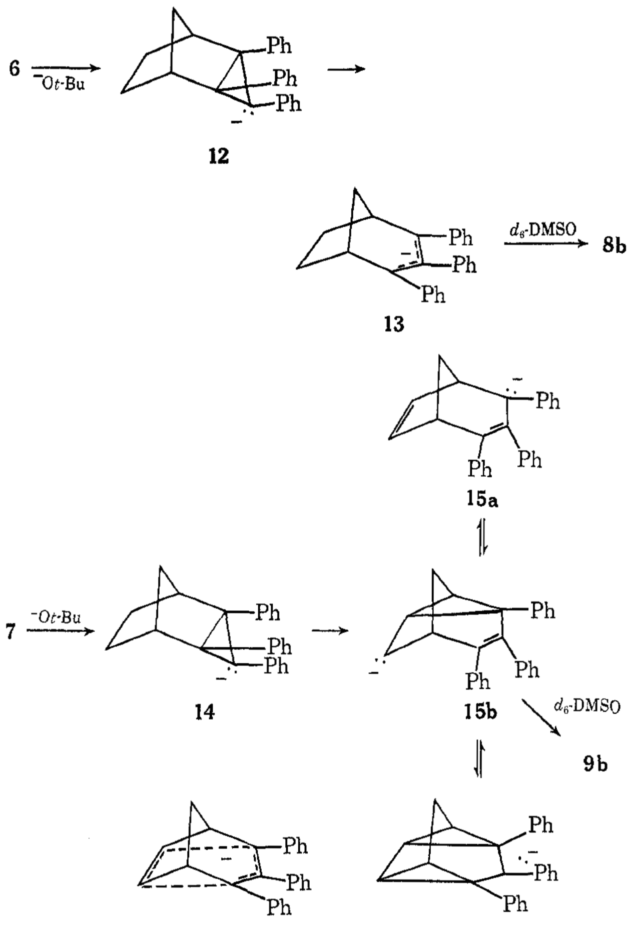
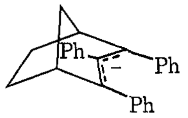
It appears that both products **8** and **9** arise by abstraction of a benzylic cyclopropyl proton from **6** and **7**, respectively, followed by an apparent disrotatory ring opening as shown in Scheme I.

SCHEME I

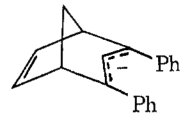


It should be noted that, when reactions 1 and 2 are carried out in the absence of KO-*t*-Bu, the starting materials are recovered unchanged.

A conrotatory opening of anion **12** or **14** would result in the formation of the highly strained *trans*-allylic anions **13a** or **15e** which could rapidly isomerize to **13** and **15**, respectively. Although *trans*-cycloheptenone is known[14] as a reactive intermediate, there are no



13a



15e

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(10) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1967, p 132.

(11) H. Prinzbach and H. D. Martin, *Helv. Chim. Acta*, **51**, 438 (1968).

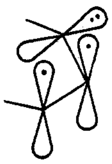
(12) A footnote in a recent paper[13] mentions that Li-$NH_2CH_2CH_2NH_2$-catalyzed conversion of **7** to **9a** at 100°. Details are not given.

(13) W. Eberbach and H. Prinzbach, *Chem. Ber.*, **102**, 4164 (1969).

(14) E. J. Corey, M. Tada R. La Mahieu, and L. Libit, *J. Amer. Chem. Soc.*, **87**, 2051 (1965).

examples of trans olefinic bonds in six-, or less, membered rings and, although **13a** and **15e** cannot be dismissed as possible intermediates, they would be quite extraordinary.

If anion **12** or **14** is opened in a disrotatory mode, this would be an apparent violation of the Woodward–Hoffmann rules.[4] However the concerted nature of the ring opening has not been proven. For example, ring opening could occur to give a nonplanar undelocalized carbanion (but still phenyl delocalized) as indicated in **16**.



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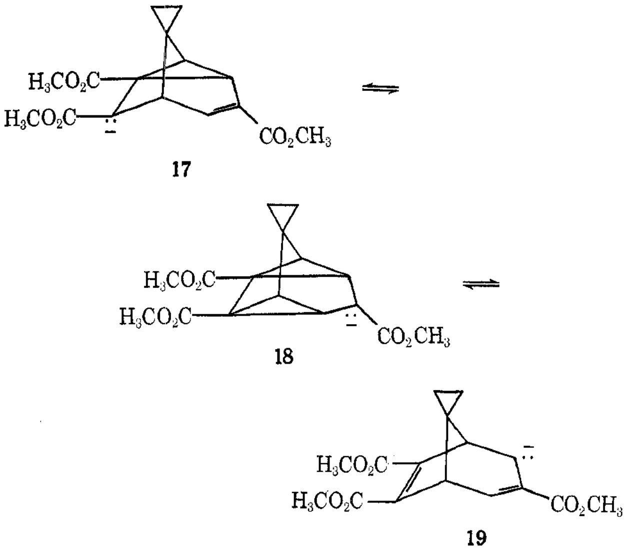
Anions **15a, b, c** are written as an equilibrium mixture, rather than as a single delocalized bishomocyclopentadienyl anion (**15d**). Although the unphenylated anion corresponding to **15d** has clearly been shown to be delocalized,[15] we observe that, when quadricyclane **11** is treated with KO-*t*-Bu–d_6-DMSO, the only product recovered is the monodeuterated (at the 3 position) quadricyclane. If **11** and **7** were to yield a common intermediate, **15d**, the same products would be expected after the prolonged equilibration times in these experiments.

It should be noted that a tricarbomethoxylated derivative of anion **15** has been proposed to exist as an equilibrium mixture of discrete ions **17–19**.[13]



The isolation of compound **9** after 20-hr reaction time may indicate that **9** is the most thermodynamically stable of the isomers **9**, **10**, and **11**. There is precedent for this in the case of the unphenylated ion[16] as well as in the case of a tricarbomethoxylated derivative of the anion.[13,17]

A comparison of the rate of reaction of **6** and **7** with KO-*t*-Bu in d_6-DMSO is expected to help clarify the nature of the anions derived from these materials.

Experimental Section

Carbon and hydrogen microanalyses were performed by the Micro-Tech Laboratories, Skokie, Ill., or Huffman Laboratories, Inc., Wheatridge, Colo. Deuterium analyses reported as "deuterium atom per molecule" were calculated from mass spectral data. Deuterium analyses reported in this manner and all other molecular weight data were obtained using a Hitachi Perkin-Elmer RHU-6E mass spectrometer. Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Reagent grade dimethyl sulfoxide was refluxed over calcium hydride 1 hr prior to final distillation.

Matheson Coleman and Bell practical grade potassium *tert*-butoxide was used without further purification.

Dimethyl sulfoxide (99.5 atom % deuterium) was obtained from Stohler Isotope Chemicals.

Potassium *tert*-butoxide reactions were run under a nitrogen atmosphere in flame-dried apparatus protected by calcium chloride drying tubes.

Preparation of 2,3,4-Triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]-6-octene (7).—The procedure was adopted from a communication by Battiste.[18] A solution of 1,2,3-triphenylcyclopropene (1.0 g, 0.0037 mol) and freshly distilled cyclopentadiene (8.0 g, 0.12 mol) was stirred at room temperature for 16 hr. At the end of this time, the excess diene had evaporated and the remaining white solid was recrystallized twice from 95% ethanol to give 0.80 g (65%) at 2,3,4-triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]-6-octene (**7**) as small white needles, mp 162–164° (lit.[18] mp 160–162°). The nmr spectrum was in complete accord with the literature spectrum.

Preparation of Dipotassium Diazocarboxylate.—This compound was prepared in 81% yield by the procedure of Thiele.[19]

Preparation of 2,3,4-Triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]octane (6).—The procedure was adopted from a communication by Battiste.[18] To a solution of 2,3,4-triphenyl-*endo*-tricyclo-[3.2.1.0^{2,4}]-6-octene (**7**, 1.0 g, 0.0030 mol) in a mixed solvent of dimethoxyethane (30 ml) and methanol (10 ml) were added dipotassium diazocarboxylate (2.0 g, 0.010 mol) and several drops of glacial acetic acid. The solution was stirred at room temperature until all of the diazo compound had been consumed (3 hr). The reaction mixture was diluted with water and extracted with ether. The combined organic layers were dried over sodium sulfate. Removal of the solvent and recrystallization from 95% ethanol gave 0.95 g (95%) of 2,3,4-triphenyl-*endo*-tricyclo-[3.2.1.0^{2,4}]octane (**6**) as shiny white plates, mp 151–152° (lit.[18] mp 149–150.5°). The nmr spectrum was in complete accord with the literature spectrum.

Reaction of 2,3,4-Triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]-6-octene (7) and Potassium *tert*-Butoxide in DMSO.—Potassium *tert*-butoxide (1.02 g, 0.0092 mol) was added to a solution of 2,3,4-triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]-6 octene (**7**, 0.84 g, 0.0025 mol) in DMSO (12 ml) with stirring under nitrogen. The deep red reaction mixture was stirred at 70° for 20 hr, after which the solution was diluted with water and extracted with ether. The ether layer was dried over sodium sulfate. Removal of the solvent and recrystallization from 95% ethanol afforded 0.63 g (75%) of 2,3,4-triphenyltricyclo[3.2.1.0$^{2',7'}$]-3-octene (**9a**), mp 157–158°. The uv spectrum in 95% EtOH had λ_{max} 277 nm (ϵ 11,300). The nmr spectrum (CDCl$_3$) featured the following resonances (peak assignments tentative in some cases): aromatic multiplet centered at τ 3.1 (15 H); allylic bridgehead proton C$_5$ at 6.9, multiplet; equivalent methylenes at C$_6$ and C$_8$, multiplet centered at 8.1; cyclopropyl hydrogens centered at 8.6. The unsaturation test with bromine was positive while that with permanganate was negative. Vpc analysis (5-ft SE-30, 225°) of the crude reaction mixture and the ether extract showed only the tricyclic product **9a**. It should be noted that it was possible to separate an authentic mixture of 2,3,4-triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]-octene (**7**) and 2,3,4-triphenyltricyclo[3.2.1.0$^{2',7'}$]-3-octene (**9**) on this column.

Anal. Calcd for C$_{26}$H$_{22}$: C, 93.42; H, 6.58; mol wt, 334. Found: C, 93.39; H, 6.67; mol wt (mass spectrum), 334.

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[15] (a) J. M. Brown and J. L. Occolowitz, *Chem. Commun.*, 376 (1965); J. M. Brown, *ibid.*, 639 (1967); J. M. Brown and J. L. Occolowitz, *J. Chem. Soc. B*, 411 (1968). (b) S. Winstein, M. Ogharuso M. Sakai and J. M. Nicholson, *J. Amer. Chem. Soc.*, **89**, 3656 (1967).

[16] S. Winstein, *Chem. Soc. Spec. Publ.*, No. 21, 5 (1967).

[17] H. Prinzbach, W. Eberbach, M. Klaus, and G. Veh, *Chem. Ber.*, **101**, 4066 (1968).

[18] M. A. Battiste, *Tetrahedron Lett.*, **No. 50**, 3795 (1964).

[19] J. Thiele, *Ann.*, **271**, 127 (1892).

When this reaction was carried out under the same conditions in d_6-DMSO, the same product was obtained except that it contained 1.50 D/molecule.

Reaction of 2,3,4-Triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]octane (6) with Potassium *tert*-Butoxide in DMSO at 70°.—Potassium *tert*-butoxide (1.00 g, 0.009 mol) was added to a solution of 2,3,4-triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]octane (6, 0.79 g, 0.0023 mol) in DMSO (15 ml) with stirring under nitrogen. The reaction mixture became deep green after a few minutes and the solution was stirred at 70° for 20 hr. The solution was diluted with water and extracted with ether. The ether layer was dried over sodium sulfate. Removal of the solvent and recrystallization from 95% ethanol yielded 0.67 g (85%) of 2,3,4-triphenylbicyclo[3.2.1]-2-octene (8a), mp 151–154°. The uv spectrum (95% EtOH) had λ_{max} 258 nm (ϵ 9680). The nmr spectrum ($CDCl_3$) featured the following resonances: aromatic multiplet centered at τ 3.00 (15 H); benzyl proton at 6.25 (1 H) as a doublet (J = 2 Hz); stilbenyl bridgehead as a multiplet at 7.1 (1 H); the other bridgehead proton at 7.65 (1 H) as a multiplet; a multiplet centered at 8.15 (4 H) assigned to methylene proton anti to the double bond, the two protons of C-7 and the exo proton at C-6; a multiplet at 8.75 (2 H) assigned to the methylene proton syn to the double bond and the endo proton of C-6. Unsaturation tests (bromine and permanganate) were negative.

Glpc analysis (5-ft SE-30, 225°) of the crude reaction mixture and the ether extract showed only the bicyclic product (8a). It should be noted that it was possible to separate an authentic mixture of 2,3,4-triphenyl-*endo*-tricyclo[3.2.1.0^{2,4}]octane (6) and 2,3,4-triphenylbicyclo[3.2.1]-2-octene on this column.

Anal. Calcd for $C_{26}H_{24}$: C, 92 85; H, 7.15; mol wt, 336. Found: C, 92.61; H, 7.26; mol wt (mass spectrum), 336.

When the reaction was carried out under the same conditions in d_6-DMSO the same product was obtained except that it contained 0.98 D/molecule. The low field signal at τ 6.25 due to the allylic proton at C-4 was absent.

Preparation of Triphenylbishomocyclopentadiene (11).—The procedure was adopted from Prinzbach and Martin.[11] In a sealed tube under nitrogen, 2,3,4-triphenyl-*endo*-tricyclo-[3.2.1.0^{2,4}]-6-octene (7, 3.0 g, 0.00896 mol) was heated at 190° for 24 hr. The green-black solid was recrystallized three times from 95% ethanol to give 0.9 g (30%) the quadricyclane 11 as white crystals, mp 138–141°. The nmr and uv spectra were in complete accord with the literature spectra.

Reaction of Triphenylbishomocyclopentadiene (11) with Potassium *tert*-Butoxide in d_6-DMSO.—Potassium *tert*-butoxide (0.63 g, 0.0056 mol) was added to a solution of the quadricyclane 11, 0.50 g, 0.00149 mol) in d_6-DMSO (15 ml) with stirring under nitrogen. The orange-red solution was stirred for 20 hr at 70° after which the solution was diluted with water and extracted with ether. The ether layer was dried over sodium sulfate. Removal of the solvent and recrystallization from 95% ethanol gave 0.45 g (90%) of the quadricyclane 11, mp 138–141°. The nmr spectrum was identical with that of the starting compound except for the absence of the benzyl proton. A mixture melting point with an authentic sample was not depressed.

Anal. Calcd for $C_{26}H_{21}D$: C, 93.13; H, 6.87; mol wt, 335. Found: C, 93.40; H, 6.69; mol wt (mass spectrum), 335; 1.01 deuterium atom per molecule.

Registry No.—**6,** 906-84-3; **7,** 906-85-4; **8a,** 34934-84-4; **9a,** 34922-26-4; **11,** 34938-92-6.

Linear Free-Energy Relationships among Reactions Occurring on the Cyclohexyl Ring. The Bromination of C_4-Substituted Cyclohexanones

J. L. Mateos,[1a] H. Flores,[1a] and H. Kwart*[1b]

Facultad de Quimica de la Universidad Nacional Autonoma de Mexico,
and the Department of the University of Delaware, Newark, Delaware 19711

Received June 8, 1970

The rates and activation parameters in bromination of C_4-substituted cyclohexanones under various reaction conditions show very little change with large variation in the nature of the remote substituent. It is shown that these exceedingly small rate effects are to be reconciled with factors inherent in the enolization mechanism of bromination. The effort to apply these rate data in a linear free-energy relationship with corresponding data for ArSCl addition and $NaBH_4$ reduction reactions occurring at a ring atom in C_4-substituted cyclohexyl derivatives has afforded some understanding of the factors which vitiate correlations of this nature.

In earlier investigations[2,3] examples were cited which indicated that in some instances conformational influences of remote substituents as well as polar effects govern the reaction rates. In one such example[3] the conclusion was drawn that a given substituent may influence the competing rate processes differentially. Thus, in the reduction of 4-substituted cyclohexanones it was shown that the substituent may exert a different influence on the transition state for reduction to a cis alcohol than in the transition state for reduction to a trans. It is conceivable, however, that cases can exist in which a given 4 substituent regulates a (common) transition state *via* two different but simultaneously active influences, namely conformational and polar. These influences, furthermore, could be considered as separable and correlatable in a linear free-energy relationship. Equation 1 may be proposed as a

$$\log k_a = (m\sigma_c + n\sigma_p)\rho_a \qquad (1)$$

possible expression for correlating such conformational and polar effects exercised simultaneously in a given transition state. Here k_a is the rate constant for the reaction a under study, σ_c and σ_p are the substituent constants expressing, respectively, the conformational and polar effects of substituents, and m and n are weighing factors related to the nature of both the substituents and the reaction under study. The parameter ρ_a has the usual significance of the reaction constant.

For the addition of ArSCl to 4-substituted cyclohexenes[2a] polar effects dominate, and it has been found that

$$(m\sigma_c + n\sigma_p) \cong n_2\sigma_p = \sigma_I \qquad (2)$$

where σ_I is the familiar inductive substituent constant,[4] reducing to the situation prevailing in rigid, bicyclic

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(1) (a) Facultad De Quimica, Universidad Nacional Autonoma De Mexico 20, D. F.; (b) Department of Chemistry, University of Delaware, Newark, Del.

(2) (a) H. Kwart and L. J. Miller, *J. Amer. Chem. Soc.*, **83**, 4552 (1961). (b) H. Kwart and T. Takeshita, *ibid.*, **84**, 2833 (1962). (c) Much of the rate data for the ArSCl addition reactions and $NaBH_4$ reductions applied in various plots in this article have been taken from the Ph.D. dissertation of S. Hsia, University of Delaware, June 1967. A publication discussing this work is presently in preparation. (d) The results of A. A. Khan from these laboratories to be discussed in a future article.

(3) H. Kwart and T. Takeshita, *J. Amer. Chem. Soc.*, **86**, 1161 (1964).

(4) R. W. Taft and I. C. Lewis, *ibid.*, **80**, 2436 (1958).