Effect of Aryl Substituents on 2-Aryl-1,4,5,6,7,7-hexachloronorbornadiene-Quadricyclane Reversible Isomerization

Hideo TOMIOKA,* Yukinobu HAMANO, and Yasuji IZAWA
Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514
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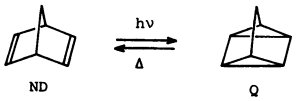
Synopsis. 2-Arylhexachloronorbornadiene undergoes photoisomerization to the corresponding quadricyclane, which returns back to the norbornadiene upon heating without catalyst. Effect of aryl substituents on the thermal reversion suggests that both spin delocalization and polar effect equally contribute to the stabilization of the transition state.

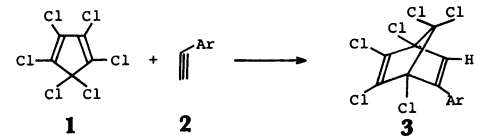
The norbornadiene (ND)-quadricyclane (Q) reversible isomerization is an attractive model system for the chemical conversion of light energy.[1] Energy is stored when norbornadiene is converted photochemically to the higher energy quadricyclane. The energy is



released when quadricyclane is (catalytically) converted back to norbornadiene. Since norbornadiene itself does not undergo efficient valence isomerization upon direct and/or sensitized irradiation, norbornadienes bearing an appropriate chromophore have been synthesized and their photoisomerization has been examined.[2] The properties of quadricyclanes derived from these norbornadienes are also quite important in connection with the design of the system and hence the heat and the rate of the reversion of the quadricyclanes to the starting compounds are measured which provides an important information on the mechanism of the reversion.[3] As a part of such studies we synthesized 2-arylhexachloronorbornadienes and investigated the effect of aryl substituents on the reversible isomerization.

Results and Discussion

The norbornadienes (**3**) were synthesized[4,5] by the Diels-Alder addition between hexachlorocyclopentadiene (**1**) and arylacetylenes (**2**) bearing electron-donating and withdrawing groups in refluxing



1 **2** **3**

Ar=X- C_6H_4 **a**: X=4-MeO, **b**: X=4-Me, **c**: X=H, **d**: X=4-Br, **e**: X=3-Br

toluene. These norbornadienes (**3**) were easily purified by vacuum distillation followed by recrystallization from hexane with exception of the methoxy derivative (**3a**). Irradiation of **3** in Pyrex tube with high-pressure Hg lamp gave the corresponding quardricyclanes (**4**) in quantitative yield. Quantum yield of the photocycloaddition with 313 nm light was 0.42 for **3c**.

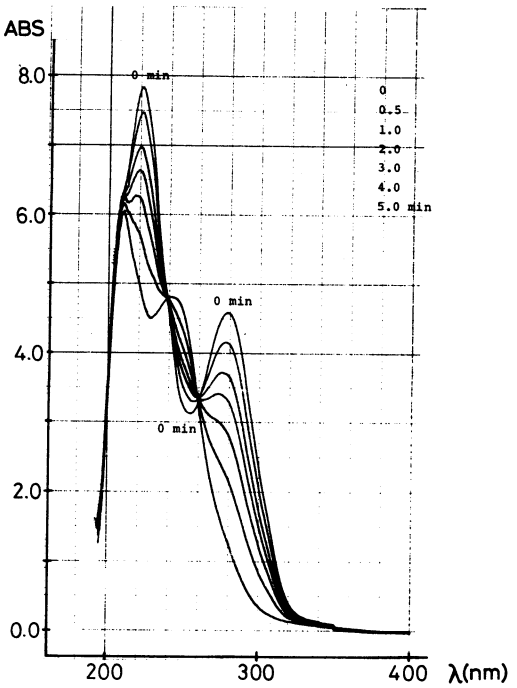
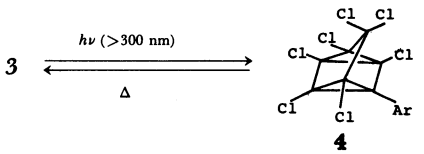


Fig. 1. UV spectra of the photoisomerization of **3c** to **4c**. A carbontetrachloride solution of 1.4×10^{-4} M **3c** was irradiated with 313 nm light.



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Quadricyclanes returned back to the norbornadienes quantitatively upon heating in carbon tetrachloride without catalyst. UV spectra of the photoisomerization of **3c** to **4c** was shown in Fig. 1, which shows the isosbestic point at 238 and 260 nm, indicating the quantitative isomerization of **3c**. UV spectra of the thermal reaction of **4c** to **3c** was superimposable to that of the photoisomerization, again indicating the quantitative isomerization of **4c**. Thus, photoisomerization and thermal back process were completely reversible. The heat of reversion (ΔH) of **4c** to **3c** was 21.6 kcal mol^{-1} (1 cal=4.184 J). The rate constants for the reversion at 60.0 °C were measured by monitoring a ^1H NMR spectra and appear in Table 1 along with Arrhenius parameters.

It has been suggested[3f] that the thermal isomerization of quadricyclanes proceeds via diradical mechanism. While rate constants in Table 1 do not show the wide range distribution that many cationic reactions do, nonetheless there are discernible differences. However, there is no single substituent constant that corre-

Table 1. Rate Constants and Activation Parameters for Thermal Isomerization of **4** to **3**

4	X	k[a)]	E_a[b)]	S[b)]
		$10^3\ s^{-1}$	kJ mol^{-1}	J K^{-1} mol^{-1}
a	4-MeO	58.5	85.8	−20.3
b	4-Me	51.7	91.2	−5.0
c	H	58.8	106.7	42.3
d	4-Br	105.3	98.3	22.4
e	3-Br	73.9	96.2	13.3

a) All rates were measured in CCl_4 at 60 °C. b) These values are each based on 3 runs at temperature between 50 and 60 °C.

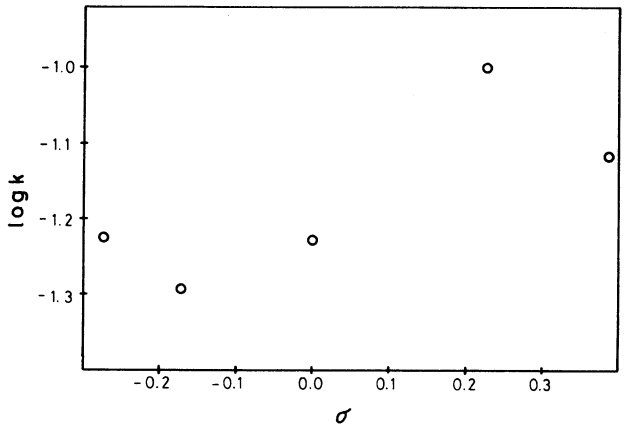

Fig. 2. A plot of relative rate constants for **4**→**3** isomerization at 60.0°C vs. Hammett σ value.

lates all of the data. The effects of substituents on radical stability is not as well understood as in carbocationic reactions. One problem is the separation of true radical-stabilizing effects from polar effects which are known to operate in many radical reactions. Many radical reactions correlate with Hammett σ (σ^+) constants,[6] because of the magnitude of polar effects. No correlation of all the data in Table 1 could be obtained, however, with σ (σ^+) values. On the other hand, various free radical substituent constants ($\sigma\cdot$) have been proposed[7] to separate the polar factors from true free radical stabilizing effects. Attempts to correlate the present data with $\sigma\cdot$ also gave low correlation coefficients.

Recently, a two-parameter Hammett relationship (Eq. 1) has been introduced[7] to evaluate the relative

$$\log k_{rel} = \rho\cdot\sigma\cdot + \rho\sigma \quad (1)$$

importance of radical stabilization vs. polar effects in radical reaction. In this treatment, the data are plotted against two-parameters so as to obtain the best correlation by adjusting the ratio of $\rho\cdot/\rho$ which in turn indicates the relative importance of the radical nature at the transition state. If the value of $\rho\cdot/\rho$ is low, spin delocalization of the intermediates is unimportant and an early transition state, influenced by polar factor, is suggested. If this value is high, the transition state should have radical charactor and polar factors should be relatively unimportant. Using four data available, the best correlation is obtained when the ratio of $\rho\cdot/\rho$

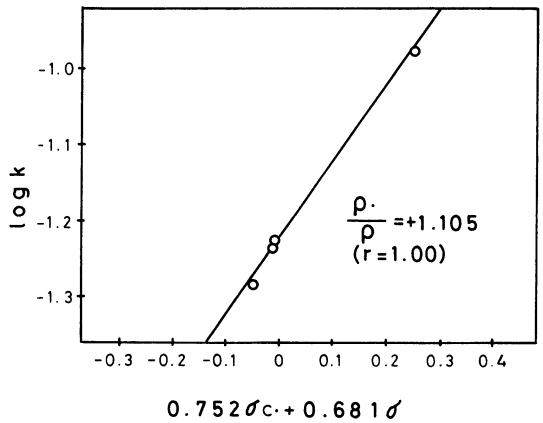

Fig. 3. A plot of relative rate constants for **4**→**3** isomerization vs. two parameters σ and σ_C.

is setted to be 1.105. This indicates that both spin delocalization and polar factors equally contribute to stabilizing the transition state for the thermal isomerization of **4** to **3**.

Thus, the photoisomerization of **3** could be possible with light of wavelength between 300—366 nm, while the heat stored in **4** is as much as that in the parent quadricyclane. Moreover, **4** is fairly stable at room temperature but is easily reverted back to **3** upon heating without catalyst. Finally it should be mentioned that the hexachloro derivatives **3** described in this paper can be prepared much more easily and are much more stable than 2-phenylnorbornadienes, which was synthesized[8] by the Diels-Alder reaction of cyclopentadiene and α-bromostyrene, followed by elimination of HBr by pottasium *t*-butoxide and decomposed slowly upon standing. Moreover, 2-phenylnorbornadiene-quadricyclane isomerization is not completely reversible.

Experimental

General. All melting and boiling points were uncorrected. UV spectra were recorded on a Hitachi 220-S spectrophotometer. IR spectra were measured on a JASCO IR-G recording spectrometer, and ^{1}H NMR spectra were determined with JEOL JNM-MH-100 NMR spectrometer in CCl_4 with Me_4Si as an internal reference. Mass spectra were recorded on Shimadzu QP-1000 mass spectrometer (70 eV). The heat of isomerization was measured on Rigaku Thermoflex Differential Scanning Calorimeter which was calibrated with KNO_3 standard. Quantum yields were determined using pottasium trioxalatoferrate (III) as an actinometer.

Material. 2-Arylhexachloronorbornadienes were prepared according to the procedure of Fry.[4a] Thus, arylacetylene (0.1 mol) and hexachlorocyclopentadiene (0.1 mol) were dissolved in dry toluene, and the solution refluxed for 3 days. After toluene was removed at the rotary evaporator, the dark brown residue was distilled at reduced pressure to give a viscous oil. A small portion of this oil was triturated with hexane at −10 °C, whereupon it crystallized, with exception of the methoxy derivative (**3a**). The remainder of the adduct was seeded with these crystals, followed by recrystallization from hexane. The data are shown below.

3a: Yield 19%; Bp 123—150 °C/0.4 mmHg (1 mmHg≈ 133.322 Pa); ^{1}H NMR (CCl_4) δ=7.15 (2H, d), 6.80 (2H, d), 6.40 (1H, s), 3.80 (3H, s); MS (70 eV) *m/z* (rel intensity, %) 401

(M^+, 17.2), 403 (M+2, 33.0), 405 (M+4, 28.9), 407 (M+6, 12.1), 367 (base peak).

3b: Yield 49%; Bp 158—160 °C/0.3 mmHg; Mp 80—81 °C; ^{1}H NMR (CCl_4) δ=7.01 (4H, bs), 6.32 (1H, s), 2.31 (3H, s); MS (70 eV) m/z (rel intensity, %) 386 (M^+, 6.3), 388 (M+2, 11.6), 390 (M+4, 9.6), 392 (M+6, 4.1), 317 (base peak).

3c: Yield 25%; Bp 123—124 °C/0.5 mmHg; Mp 94—96 °C; ^{1}H NMR (CCl_4) δ=7.30 (5H, bs), 6.50 (1H, s); MS (70 eV) m/z (rel. intensity) 372 (M^+, 7.9), 374 (M+2, 15.2), 376 (M+4, 11.8), 378 (M+6, 5.4), 303 (base peak).

3d: Yield 34%; Bp 60—62 °C/3 mmHg; Mp 76—77 °C; ^{1}H NMR (CCl_4) δ=7.50 (2H, d), 7.15 (2H, d), 6.57 (1H, s); MS (70 eV) m/z (rel intensity) 450 (M^+, 5.3), 452 (M+2, 14.5), 454 (M+4, 17.2), 456 (M+6, 11.3), 303 (base peak).

3e: Yield 39%; Bp 150—152 °C/3 mmHg; Mp 93—94 °C, ^{1}H NMR (CCl_4) δ=7.45—7.18 (4H, m), 6.59 (1H, s); MS (70 eV) m/z (rel intensity) 450 (M^+, 5.9), 452 (M+2, 15.8), 454 (M+ 4, 17.8), 456 (M+6, 10.4), 303 (base peak).

Photoisomerization of 3 to 4. A solution of **3** (100 mg) in hexane (30 ml) was prepared under an argon atmosphere in Pyrex tubes and was irradiated with a 300-W high-pressure mercury lamp at 10 °C. After irradiation for 5 h, the solvent was evaporated under reduced pressure to leave syrupy oil. Attempts to obtain the quadricyclanes (**4**) in pure forms either by recrystallization or by chromatography were unsuccessful since **4** was always contaminated with **3** due to the thermal back reaction during the work-up even at room temperature. The ^{1}H NMR data of **4** are shown below.

4a: ^{1}H NMR (CCl_4) δ=7.60 (2H, d), 7.18 (2H, d), 3.80 (3H, s), 3.10 (1H, s).

4b: ^{1}H NMR (CCl_4) δ=7.10 (4H, bs), 2.30 (3H, s), 3.08 (1H, s).

4c: ^{1}H NMR (CCl_4) δ=7.27 (5H, bs), 3.02 (1H, s).

4d: ^{1}H NMR (CCl_4) δ=7.53 (2H, d), 7.10 (2H, d), 3.18 (1H, s).

4e: ^{1}H NMR (CCl_4) δ=7.60—7.20 (4H, m), 3.20 (1H, s).

Kinetic Measurement. The rates of thermal back reaction of **4** to **3** were measured in carbon tetrachloride by monitoring ^{1}H NMR spectra. Thus, CCl_4 solution of **3** containing anisole as an internal standard was placed in Pyrex NMR tubes and was irradiated until almost all of **3** were converted to **4**. The tubes were then immersed in a water bath thermostated at a constant temperature (±0.1 °C). The rates were easily measured by monitoring the disappearance of methine proton of **4** at around 2.0 ppm and/or appearance of vinyl proton of **3** at around 6.5 ppm.

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