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Solvolysis of 1-Quadricyclylcarbinyl 3,5-Dinitrobenzoate

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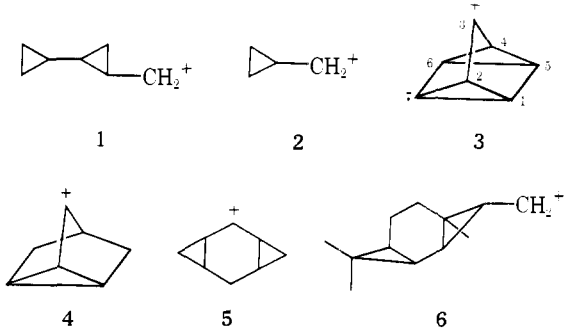
Abstract: 1-Quadricyclylcarbinol (**8b**) was synthesized from 2-norbornadienylcarbinyl acetate (**9c**), and 3,5-dinitrobenzoate of **8b** was solvolyzed in 60% aqueous acetone at 25° to yield three isomeric alcohols, **9b**, **10b**, **11b**, and three isomeric dinitrobenzoates, **9a**, **10a**, **11a**. 1-Quadricyclylcarbinyl 3,5-dinitrobenzoate (**8a**) solvolyzed 120 million times faster than cyclopropylcarbinyl 3,5-dinitrobenzoate. The extremely great stabilization of 1-quadricyclylcarbinyl cation was explained by the strain relief (70–75%) and the cyclopropyl-cyclopropyl interaction (25–30%). The charge delocalized form **15** derived from the cyclopropyl-cyclopropyl interaction (characterized by MO calculations) satisfactorily explained the product distribution.

The remarkable facility of cyclopropane rings to stabilize carbonium ions has attracted much attention of organic chemists.[1] Experimental and theoretical approaches have clarified that the great stabilization is attained by a conjugation between the vacant p orbital at the carbinyl carbon and $sp^{4.1}$[2] hybrid orbital in the plane of cyclopropane.[1b]

However, little attention has been given to systems endowed with a possibility of cyclopropyl-cyclopropyl interaction[2] despite its great theoretical interest and the extensive structural variations possible. An extra stabilization, if any, of a generalized ionic system (**1**) compared with cyclopropylcarbinyl cation (**2**) is attributable to the assumed cyclopropyl-cyclopropyl interaction. Thus, 3-quadricyclyl *p*-bromobenzenesulfonate (3-OBs) solvolyzes only 15 times faster

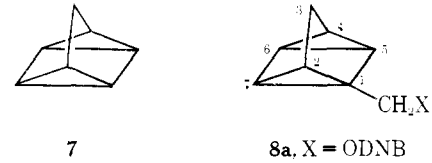


1 2 3

4 5 6

than the corresponding nortricyclyl derivative (4-OBs).[3] However, that 3-OBs is only two to three times more reactive than cyclopropylcarbinyl-OBs[4] implies that no significant assistance is attained by the introduction of cyclopropyl of inappropriate arrangement in **3**, in contrast to the energetically additive effect observed for cyclopropyl rings in bis(cyclopropyl)carbinyl systems such as **5**.[5] No or little extra stabilization was observed for the system **6**.[4b] The cyclopropyl-cyclopropyl interaction, therefore, has no significant contribution to the stabilization of **3**, **5**, or **6**. From their theoretical approaches, Wilcox et al.[6] discussed poor transmission of substituent effect of the cyclopropyl rings on stabilization (or destabilization) of **2**.

The regiospecificity and stereospecificity of the cycloaddition reaction of quadricyclane (**7**)[2a] with dienophiles, however, are best interpreted by an unusually effective cyclopropyl-cyclopropyl interaction in quadricyclane (**7**) especially in a transition state. The interaction energy estimated as the level splitting of cyclopropane ring bonds amounted to ca. 0.6 eV (from MINDO/1 calculation), although some basic properties[7] of **7** in its ground electronic



7

8a, X = ODNB
b, X = OH
c, X = OAc

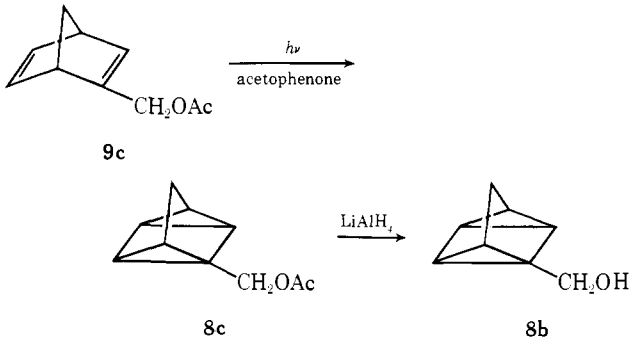
state have the value of normal cyclopropane. It seems quite likely that only the arrangement of the two cyclopropane rings in nearly parallel and in close proximity afforded such

an unique electronic state as quadricyclane type, and the interaction may increase in a transition state where some relatively strong perturbation is given.

In this article, the authors report an extremely high solvolytic reactivity of 1-quadricyclylcarbinyl 3,5-dinitrobenzoate (**8a**) (ODNB ≡ 3,5-dinitrobenzoate). Participation of the two ideally fixed cyclopropyl rings to the carbinyl carbon was attained in ionization of **8a**. Strain relief (70–75%) due to loosening of the cyclopropyl ring bond and quadricyclyl type interaction (due to fixed cyclopropyl) (25–30%) are presented to account for the extremely great acceleration of the present solvolysis. Much poorer stabilization of 3-quadricyclyl cation (**3**) compared with nortricyclyl (**4**) is discussed.

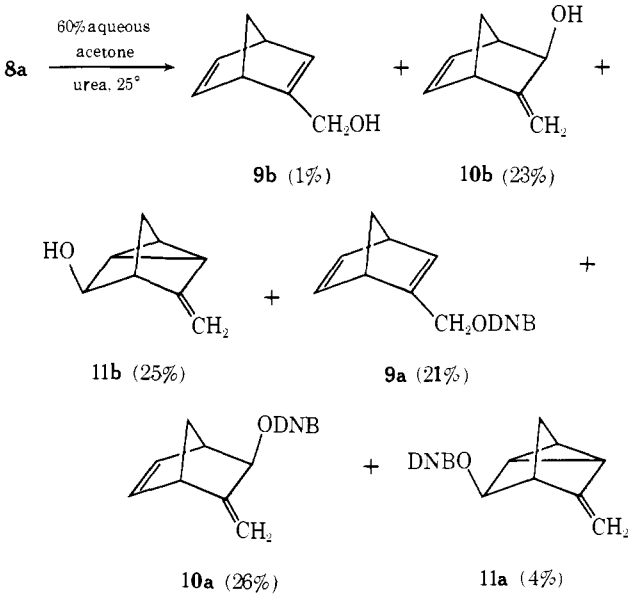
Results and Discussion

1-Quadricyclylcarbinol (**8b**) was prepared by acetophenone-sensitized irradiation of 2-norbornadienylcarbinyl acetate[8] (**9c**), followed by a treatment with lithium aluminum hydride. Esterification of the carbinol (**8b**) with 3,5-dinitrobenzoyl chloride in pyridine and methylene chloride gave 1-quadricyclylcarbinyl 3,5-dinitrobenzoate (**8a**). That no detectable isomerization accompanied the esterification was ascertained by the NMR spectrum of **8a**.



9c 8c 8b

Solvolytic Studies. Solvolysis was conducted for 1-quadricyclylcarbinyl-ODNB (**8a**) in 0.01 *M* urea-buffered 60% aqueous acetone. The dinitrobenzoate completely disappeared in ca. 10 min at room temperature, giving three isomeric alcohols, **9b** (1%), **10b** (23%), **11b** (25%), and three isomeric dinitrobenzoates, **9a** (21%), **10a** (26%), **11a** (4%).



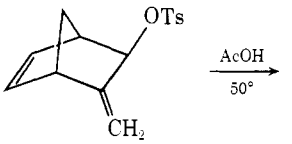
9b (1%) 10b (23%) 11b (25%) 9a (21%) 10a (26%) 11a (4%)

The alcohols produced were separated and collected by preparative GLC. The structures of three alcohols were determined by comparison of NMR and ir spectra with those of authentic samples. Authentic alcohols were prepared by $LiAlH_4$ treatment of 2-norbornadienylcarbinyl (**9c**), 3-methylene-*exo*-2-norbornenyl (**10c**), and 6-methylene-2-nortricyclyl (**11c**) acetates, respectively, the latter two of which were also obtained in acetolysis of 3-methylene-*exo*-2-norbornenyl tosylate (**10d**)[9] in the ratio of **10c:11c** = 56:44. Hydrolysis of the tosylate **10d** gave **10b** exclusively in urea-buffered 80% aqueous acetone at 40°.

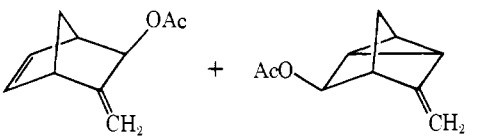
Table I. Solvolysis Rates of 1-Quadricyclylcarbinyl 3,5-Dinitrobenzoate (**8a**) and Related Dinitrobenzoates

R-ODNB	Solvent	*T*, °C	*k*, sec^{-1}	Rel *k* (100°)
8a	80%	3.5	2.08×10^{-4}	$\Delta H^{\ddagger}$ = 19.3 kcal/mol
	Acetone–H_2O	6.8	3.45×10^{-4}	$\Delta S^{\ddagger}$ = −7.3 eu
		12.8	6.65×10^{-4}	
		21.5	1.77×10^{-3}	
		100	1.93[a]	
8a	60%	100	5.19×10[b]	120,000,000
9a	50%	71.2	6.9×10^{-5}	
		80.2	1.7×10^{-4}	
9a	60%	100	2×10^{-4}	500
12	60%	100	ca. 6×10^{-8}[c]	ca. 0.15
13	60%	100		1–100[d]
14	60%	100	1.7×10^{-1}[e]	400,000[e]
6	60%	100	5.42×10^{-4}[f]	
3	60%	100	ca. 10^{-6}[c]	2–3
2-ODNB	60%	100	4.3×10^{-7}[f]	1

[a] Extrapolated. [b] Calculated, assuming a factor of 26 for the solvent effect on rate in 60 and 80% aqueous acetone: A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 78, 2770 (1956). [c] Calculated, ref 1b and 3. [d] Reference 11. [e] *p*-Nitrobenzoate, ref 12. [f] Reference 4b.



10d



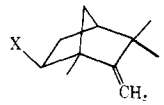
10c 11c

Authentic samples of three isomeric dinitrobenzoates **9a**, **10a**, and **11a** were prepared from authentic alcohols, **9b**, **10b**, and **11b**, respectively.

In NMR spectra of 3-methylene-*exo*-2-norbornenyl acetate (**10c**), alcohol (**10b**), and dinitrobenzoate (**10a**), protons α to oxygen adsorbed at δ 5.02, 3.95, and 5.30, respectively. No appreciable separation larger than 2 Hz in these absorptions excluded the possibility of structure of 7-methylene-*exo*-2-norbornenyl type since the resonance of the proton α to oxygen appears as a doublet of doublets ($J_{2,3}$(endo-endo) = 8 Hz and $J_{2,3}$(endo-exo) = 3 Hz) in *exo*-2-norbornenyl acetate or alcohol.[10]

To determine the rate of the rapid solvolysis, the reaction was conducted in 80% aqueous acetone by titration of the resultant 3,5-dinitrobenzoic acid with keeping pH constant. The infinity titer was 41.8% of the theoretical value, which corresponded to the portion of the hydrolyzed products among all the products. Since 2-norbornadienylcarbinyl-ODNB (**9a**) solvolyzes much more slowly (see Table I), any contribution of further solvolyses of three return products is

reasonably neglected to give the observed clean first-order kinetics. The rate constants at several temperatures are

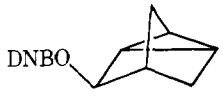


X = ODNB, Br

given in Table I together with calculated kinetic parameters. Also included for comparison are rate constants of solvolyses of related compounds.

The first thing to note was that 1-quadricyclylcarbinyl-ODNB (**8a**) was 120 million times more reactive than cyclopropylcarbinyl-ODNB (2-ODNB),[4b] the figure of which corresponded to the stabilization of the transition state by 14.0 kcal/mol. **8a** was the most reactive primary cyclopropylcarbinyl system ever reported.[1]

Rate enhancement of **8a** compared with related compounds with fragmental participation (see Table I) are 8×10^8 for nortricyclyl-ODNB (**12**) and 10^6-10^8 times for 6-methylene-*exo*-2-norbornyl-ODNB (**13**),[11] respectively.



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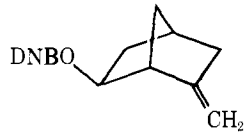

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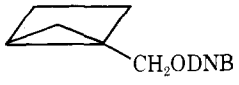
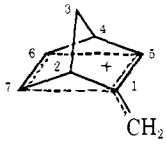
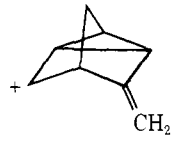


14

Even 1-bicyclo[2.1.0]pentylcarbinyl-ODNB (**14**) was much less reactive than **8a**. Furthermore, the successful isolation of 6-methylene-2-nortricyclyl-ODNB (**11a**) as a return product indicated that **11a** was much less reactive than **8a** in the solvolysis. Therefore, it is obvious that all of the component structures, the first cyclopropyl ring or the double bond and the second cyclopropyl ring, are important for stabilization of the transition state of **8a** like **15**. It is not out of



15



16

bounds of possibility that other cations than **15** might be involved (in the hydrolysis). An alternative cation **16** (delocalized), as the most probable candidate, might have the important contribution to the present case. However, hydrolysis of tosylate **10d** gave alcohol **10b** exclusively. The delocalized **16** would be the most plausible intermediate in this case. Cation **16**, therefore, seems to differ from present 1-quadricyclylcarbinyl cation which is most probably depicted as **15**, and the contribution of **16** would not be very important to the hydrolysis of 1-quadricyclylcarbinyl system.

In preliminary conclusion, therefore, only the ideally fixed system like 1-quadricyclylcarbinyl can gain enormously great stabilization in ionization (presumably through delocalized ion **15**), and systems of **10a** and **11a** can not. This is interpreted as a result of an unique electronic state of quadricyclane type with its highest occupied

	E(eV)	symmetry
	-1.6957	20 (AA)
LUMO	-1.7452	19 (SS)
HOMO	-9.0914	18 (AS)
	-9.7102	17 (SA)
	-9.8752	16 (AA)
	-10.3933	15 (SS)

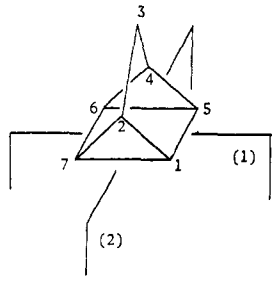
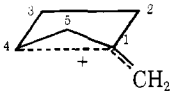


Figure 1. Selected energy level and orbital symmetry of quadricyclane[19] (MINDO/1 calculation).

molecular orbital at the remarkably high energy level (vide infra).

Effect of Strain Relief and Cyclopropyl–Cyclopropyl Interaction. The bond loosening of C_1-C_7 leading to strain relief had a significant contribution to the stabilization of **15**. The idea that the loosening of the C_1-C_7 bond in the transition state leads to the increase in rate of solvolysis was in accord with the transition-state structure (**17**) drawn by Schleyer et al.[4b] (where C_1-C_2 was loosened, and C_2-C_3 was strengthened) or with an observation by Dauben et al. that 1-bicyclo[2.1.0]pentylcarbinyl-OPNB (**14**-OPNB) solvolyzes 4×10^5 times faster than the corresponding cyclopropylcarbinyl (**2**-OPNB)[12] because of an extra extent of C_1-C_4 bond loosening in the transition state (**18**).

17



18

The substantial identity of the strain relief [40 ± 0.65 kcal/mol for 1-quadricyclylcarbinyl system,[13,14] 46 kcal/mol for 1-bicyclo[2.1.0]pentylcarbinyl system (**14**)[12,17]], as well as the close resemblance in geometry[7a] and p character[7b,c] between quadricyclane and bicyclo[2.1.0]pentane, allowed the authors to assume bicyclo[2.1.0]pentylcarbinyl-ODNB (**14**) as a model for the strain relief effect.

When the effect of the strain reliefs are assumed to be equal for systems **8a** and **14**, (at least) 300-fold increase in reactivity (Table I) of **8a** over **14** is attributed to the additional stabilization effect (4.0 kcal/mol) in the present system. Even when a larger reported value of 52 kcal/mol[14] was employed as the strain relief for 1-quadricyclylcarbinyl, an independent and quantitative argument made little alteration of our conclusion. Thus, the assumption of linear free energy relationship, $\Delta G_{\text{strain relief}} - \Delta G^{\ddagger}_{\text{strain relief}}$, between bicyclopentylcarbinyl system **14** ($\Delta G_{\text{strain relief}}$ = 46 kcal/mol, $\Delta G^{\ddagger}_{\text{strain relief}}$ = 9.79 kcal/mol) and 1-quadricyclylcarbinyl system **8a** ($\Delta G_{\text{strain relief}}$ = 52 kcal/mol) leads to a conclusion that $\Delta G^{\ddagger}_{\text{strain relief}}$ for **8a** is 11.07 kcal/mol, the minimal value of 14.0 − 11.1 = 2.9 kcal/mol being attributable to the cyclopropyl-cyclopropyl interaction.

MO calculations (MINDO/1, CNDO/2, extended Hückel methods) of quadricyclane gave satisfactorily reasonable features of both the unique electronic state of quadricyclane type and the extremely great participation of quadricyclane moiety to the carbinyl cation. The energy level of the highest occupied molecular orbital (HOMO) of quadricyclane is higher than that of cyclopropane by 1.2 eV (extended Hückel method). The extremely great participation of quadricyclane moiety to the carbinyl cation is in good accord with the idea that HOMO at the relatively high energy level can strongly interact with the vacant p orbital at the carbinyl carbon. The facile electron donation of quadricyclane was strongly supported by the quite low first

ionization potential (IP = 8.6 eV from photoelectron spectroscopy[18]). HOMO, which has AS symmetry (Figure 1), largely contributes to the bonding between $C_1(C_5)$ and $C_7(C_6)$ and to the antibonding between $C_1(C_7)$ and $C_5(C_6)$. Removal of an electron from HOMO, therefore, extremely lessens the C_1-C_7 (C_5-C_6) bonding, while the bonding interaction increases between $C_1(C_7)$ and $C_5(C_6)$. This gave a picture that the interaction between ideally fixed cyclopropyl-cyclopropyl accompanies the participation of quadricyclane moiety to the carbinyl cation, where the perturbed state mentioned above (HOMO electron withdrawal) may resemble the 1-quadricyclylcarbinyl cation depicted in **15**.

Product-Determining Step. The unique 1-quadricyclylcarbinyl cation (**15**) reacted with nucleophiles in a very interesting fashion.

The portion of the assisted products, 2-norbornadienylcarbinyl type **9a** and methylenenorbornenyl type **10a** in all the return products [(**9a** + **10a**)/(**9**, **10**, **11a**) = 0.92] was larger than that of assisted products **9b** and **10b** in the hydrolysis products [(**9b** + **10b**)/(**9**, **10**, **11b**) = 0.49]. This observation is in good accord with an idea that, in the cation (ion pair) where the participation of the nucleophiles (solvent) is restrained by a bulky, weakly nucleophilic anion to lead to the return products, much more electron is demanded by the carbinyl cation from quadricyclane moiety than in the cation (ion pair) where nucleophiles are in close proximity to participate and to afford covalently bound products. Thus, the present product distribution is in good agreement with the observations by Bartlett et al.[20] and Johnson et al.,[21] where solvolysis of 5-hexenyl nosylate in less nucleophilic solvent (HCO_2H) gives much more assisted (cyclyzed) product than in more nucleophilic solvent (CH_3CO_2H). On this basis, the formation of the 2-norbornadienylcarbinyl type product (**9a**), in remarkable amount in the returned dinitrobenzoates, is attributable to the relatively great electron supply from quadricyclane moiety to the cation to lead to returned products. This is in accord with our hypothesis that for the participation is important HOMO of quadricyclane, which shows bonding character between C_1 and C_7 (or C_5 and C_6), together with antibonding character between C_1 and C_5 (or C_6 and C_7). Thus, removal of the HOMO electrons should lead to C_1-C_7 bond breaking and C_1-C_5 bond formation in less solvated quadricyclylcarbinyl.

The remarkable difference in reactivity between 1-quadricyclylcarbinyl-ODNB (**8a**) and 3-quadricyclyl-ODNB (**3**) (Table I) is of great interest, although comparable reactivity might be expected from (nearly) the same structural components of these (ionic systems of **1**). The differed amount of the strain relief[13] in the transition state may explain the difference in reactivities. Pictures from MO calculations also give a satisfactorily reasonable explanation. The vacant p orbital at C_3 (SA symmetry) cannot interact with HOMO (AS symmetry) of quadricyclane. This strongly implies that the fixed cyclopropyl-cyclopropyl interaction mentioned before cannot be attained in 3-quadricyclyl system. Therefore, it is again easily understood that the p orbital at C_3 interacts only with one of cyclopropyl rings in **3** to constitute a system of nortricyclyl type, while p orbital at the carbinyl carbon (1-quadricyclylcarbinyl) was able to find a configuration for the maximal interaction with the HOMO.

Experimental Section

Melting points were determined in capillaries by means of a micro melting point apparatus.

Elemental analyses were performed by Microanalysis Laboratory in Pharmaceutical Sciences, Kyushu University. NMR spectra were recorded on JEOL 60-H spectrometer or on JEOL 100-H spectrometer.

1-Quadricyclylcarbinyl Acetate (8c). A solution of 9.9 g (60.3 mmol) of 2-norbornadienylcarbinyl acetate (**9c**) and 0.25 g of acetophenone in 400 ml of ether was irradiated by a 300-W high-pressure mercury lamp at 0° for 4 hr. The conversion of the photoisomerization was monitored by a disappearance of infrared absorption at 695 cm^{-1} during the isomerization. The etheral solution was dried over anhydrous magnesium sulfate, followed by a filtration. Ether was distilled off through a 20-cm Vigreux column, and the residue was distilled under the reduced pressure. **18c** was distilled out at 56–57° (4 mm): 8.11 g (82% yield); NMR δ ($CDCl_3$) 4.21 (2 H, AB quartet, J = 12 Hz), 2.10 (3 H, singlet), 2.03 (2 H, triplet), 1.8–1.3 (5 H); ir (neat) 3070, 2980, 2945, 1740, 1240, 1025 cm^{-1}; mass *m/e* (relative intensity) 166 (M + 2, 1.0), 154 (M + 1, 12.0), 164 (M, 100), 149 (26.6), 122 (156), 105 (90), 104 (204), 103 (100), 78 (126), 66 (164). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.00; H, 7.35.

1-Quadricyclylcarbinol (8b). A mixture of 5.11 g (31.1 mmol) of 1-quadricyclylcarbinyl acetate (**8c**) and 100 ml of dry ether in a 200-ml three-necked flask, equipped with a dimroth, was cooled in an ice bath under stirring. To the ethereal solution was added 0.88 g (23 mmol) of lithium aluminum hydride in several portions, followed by continuous stirring for 2 hr at room temperature. While cooling the flask in an ice bath, aqueous solution of ammonium chloride was added until the grey precipitate became completely white, and the ethereal solution was decanted. The precipitate was washed twice with 100 ml of ether, and the combined ethereal solution was dried over anhydrous magnesium sulfate. Distillation of the solution gave 2.96 g (78.2%) of 1-quadricyclylcarbinol (**8b**): bp 49–51° (2 mm); NMR δ ($CDCl_3$) 3.75 (2 H, AB quartet, J = 12 Hz), 2.04 (2 H), 1.80 (1 H, OH), 1.8–1.3 (5 H); ir (neat) 3500–3200, 3060, 2940, 1410, 1180, 1011, 840, 812 cm^{-1}; mass *m/e* (relative intensity) 124 (M + 2, 0.97), 123 (M + 1, 10.0), 122 (M, 100), 121 (53.7), 104 (78), 92 (95), 77 (100), 66 (270), 65 (112). Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.11; H, 8.21.

2-Norbornadienylcarbinol (9b). **9b** was prepared by the treatment similar to **8b** of 2-norbornadienylcarbinyl acetate (**9c**): bp 85° (12 mm); NMR δ ($CDCl_3$) 6.80 (2 H, triplet, J = ca. 1.5 Hz), 6.45 (1 H), 4.30 (2 H), 3.65 (2 H, AB quartet, J = ca. 12 Hz), 2.02 (2 H, triplet, J = ca. 1.5 Hz), 1.80 (1 H, OH); ir (neat) 3500–3200, 3060, 2950, 1400, 1300, 1260, 1070, 1008, 785, 690 cm^{-1}; mass *m/e* (relative intensity) 124 (M + 2, 0.88), 123 (M + 1, 11.1), 122 (M, 100), 121 (56.7), 104 (71.1), 92 (77.8), 91 (224), 77 (127), 66 (236), 65 (114). Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.18; 3n H, 8.24.

1-Quadricyclylcarbinyl 3,5-Dinitrobenzoate (8a). To an ice-cold solution of 1.20 g (9.8 mmol) of 1-quadricyclylcarbinol (**8b**) in 2 ml of dry pyridine and 30 ml of dry methylene chloride was added 2.50 g (10.8 mmol) of 3,5-dinitrobenzoyl chloride under N_2. After stirring for 1 hr at 0°, the reaction mixture was kept standing overnight in an refrigerator. An usual work-up gave 2.69 g (85% yield) of a crude product as yellow needles. Recrystallization from *n*-hexane gave yellow needles: mp 74–75°; NMR δ ($CDCl_3$) 9.30 (3 H), 4, 61 (2 H, AB quartet, J = 12 Hz), 2.06 (2 H), 1.9–1.5 (5 H); ir (KBr) 3110, 2950, 1724, 1630, 1548, 1288, 1170, 720 cm^{-1}; mass *m/e* (relative intensity) 318 (M + 2, 3.09), 317 (M + 1, 20.0), 316 (M, 100), 195 (178), 149 (289), 121 (842), 104 (419), 78 (192), 77 (174), 75 (154), 66 (272). Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 56.97; H, 3.82; N, 8.86. Found: C, 56.83; H, 3.70; N, 8.75.

2-Norbornadienylcarbinyl 3,5-Dinitrobenzoate (9a). Esterification procedure for 2-norbornadienylcarbinol (**9b**) was similar to that mentioned for **8b.** Recrystallization from *n*-hexane gave yellow needles: mp 76–76.8°; NMR δ ($CDCl_3$) 9.30 (3 H), 6.82 (2 H, triplet, J = ca. 1.5 Hz), 6.72 (1 H), 5.11 (2 H, doublet, J = ca. 1.5 Hz), 3.60 (2 H), 2.11 (2 H); ir (KBr) 3100, 2980, 2950, 1724, 1630, 1547, 1345, 1160, 720 cm^{-1}; mass *m/e* (relative intensity) 318 (M + 2, 2.98), 317 (M + 1, 1 19.45), 316 (M, 100), 195 (218), 149 (288), 121 (977), 105 (143), 104 (536), 103 (146), 78 (186), 77 (181), 75 (158), 66 (291). Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 56.97; H, 3.82; N, 8.86. Found: C, 56.79; H, 3.84; N, 8.67.

3-Methylene-*exo*-2-norbornenyl Acetate (10c) and 6-Methylene-2-nortricyclyl Acetate (11c). A solution of 3-methylene-*exo*-2-norbornenyl tosylate (**10d**), which was prepared from 0.80 g (6.55 mmol) of 1-quadricyclylcarbinol (**8b**) and 1.28 g (6.7 mmol) of *p*-

toluenesulfonyl chloride, in 50 ml of acetate-buffered acetic acid was heated at 50° for 15 hr. The solution was then cooled and poured into 100 ml of ice-water and extracted twice with 200 ml of ether–pentane (1:1). The combined ether–pentane solution was washed with aqueous sodium bicarbonate solution and then with concentrated aqueous sodium chloride solution.

Ether and pentane were distilled off, and the residue was analyzed by GLC. Two products (56 and 44%), which had retention times of 10.8 and 14.4 min, respectively, were collected. The structure of the former was determined by NMR and ir spectra to be 3-methylene-*exo*-2-norbornenyl acetate (**10c**): NMR δ ($CDCl_3$) 6.20 (2 H, doublet of AB quartets, J = 6, 3 Hz), 5.10 (2 H), 5.02 (1 H), 3.20 (1 H), 2.97 (1 H), 2.10 (3 H, singlet), 1.85 (2 H); ir spectrum (neat) 3070, 2990, 2950, 2870, 1740, 1370, 1320, 1240, 1025, 890, and 728 cm^{-1}.

The product which had longer retention time was 6-methylene-2-nortricyclyl acetate (**11c**): NMR δ ($CDCl_3$) 4.85 (1 H), 4.72 (2 H), 2.38 (1 H), 2.07 (3 H, singlet), 1.9–1.4 (5 H); ir spectrum (neat) 3080, 2950, 2880, 1738, 1680, 1370, 1240, 1040, 870, 795, and 680 cm^{-1}.

3-Methylene-*exo*-2-norbornenol (10b) and 6-methylene-2-nortricyclanol (11b) were prepared by the treatment of **10c** and **11c**, respectively, with lithium aluminum hydride, as described for **8b**. **10b:** NMR δ ($CDCl_3$) 6.09 (2 H), 4.97 (2 H), 3.95 (1 H), 3.12 (1 H), 2.80 (1 H), 2.05 (1 H, OH), 1.85 (2 H); ir (neat) 3500–3200, 3065, 2980, 1320, 1100, 1039, 890, 760, 720, cm^{-1}. **11b:** NMR δ ($CDCl_3$) 4.66 (2 H), 4.10 (1 H), 2.20 (1 H), 1.9–1.4 (5 H).

3-Methylene-*exo*-2-norbornenol (10b) was also obtained from hydrolysis of tosylate **10d**. A solution of 6.2 g (23 mmol) of **10d** in 110 ml of urea-buffered 80% aqueous acetone was stirred for 10 hr at 40°. After the evaporation of ca. 80 ml of acetone at reduced pressure, the residue was extracted with 2 × 100 ml of ether–pentane (1:1). The extract was washed with aqueous solution of sodium bicarbonate and then with concentrated aqueous solution of sodium chloride. GLC analysis revealed that only 3-methylene-*exo*-2-norbornenol (**10b**) was detected in the product (1.2 g, yield 44%). The alcohol was purified through preparative GLC, and its structure was determined by NMR and ir spectra.

3-Methylene-*exo*-2-norbornenyl-ODNB (10a) and 6-methylene-2-nortricyclyl-ODNB (11a) were prepared by a treatment of **10b** and **11b**, respectively, with dinitrobenzoyl chloride, as described for **8a**. **10a:** NMR δ ($CDCl_3$) 9.30 (3 H), 6.20 (2 H, double AB quartet, J = 6, 3 Hz), 5.30 (1 H), 5.07 (2 H, doublet), 3.27 (1 H), 3.09 (1 H), 1.90 (2 H); ir (neat) 3100, 2990, 2940, 1726, 1628, 1545, 1460, 1160, 970, 815, 720 cm^{-1}. **11a:** NMR δ ($CDCl_3$) 9.30 (3 H), 5.20 (1 H), 4.80 (2 H), 2.51 (1 H), 1.9–1.4 (5 H).

Solvolysis of 1-Quadricyclylcarbinyl 3,5-Dinitrobenzoate (8a). A solution of 0.509 g (1.61 mmol) of **8a** and 0.43 g (1.53 mmol) of urea in 300 ml of 60% aqueous acetone (prepared by mixing of 3 volumes of dry acetone and 2 volumes of distilled water) was stirred for 2 hr (>10 half-lives) at 25°. After the evaporation of 150 ml of acetone at reduced pressure, the residue was extracted with 4 × 100 ml of ether–pentane (1:1). The product distribution was determined by gas liquid phase chromatography and NMR spectra.

Three isomeric alcohols **9b, 10b,** and **11b** had retention times of 11.3, 7.7, and 13.5 min, respectively, on polyethylene glycol 20M column (2.5 m, 160°, H_2 carrier, 1.0 kg/cm^2). The ratio of the three alcohols was determined by relative peak areas.

Authentic alcohols, **10b** and **11b**, were independently prepared by lithium aluminum hydride treatment of corresponding acetates, which were obtained from acetolysis of 3-methylene-*exo*-2-norbornenyl tosylate (**10d**).

The ratio of three isomeric dinitrobenzoates was determined by the average of integrations of NMR peak areas repeatedly measured on JEOL 60-H and 100-H instruments.

Kinetic Experiments. To determine the rates of the rapid solvolysis reaction of **8a**, the following procedure and an apparatus were employed.

To a 100-ml beaker, which was thermostated at a given temperature, was added 31.6 mg (0.10 mmol) of **8a** in 40 ml of dry acetone. The reaction was started by an addition of 10 ml of distilled water (also thermostated). The addition was over in 10 sec. The rate was determined by a titration of 50 ml of 0.002 M solution of the dinitrobenzoate with 0.05 M sodium hydroxide solution with keeping pH constant. The infinity titer was 41.8% of the theoretical value, which corresponded to the portion of the hydrolyzed products (**9b, 10b, 11b**) among all products.

A solution of 31.6 mg (0.1 mmol) of 2-norbornadienylcarbinyl-ODNB (**9a**) and 29.0 mg of urea in 100 ml of 50% aqueous acetone was prepared and used for kinetic experiments. An aliquot (15 ml) was taken from the solution and titrated by 0.01 N sodium hydroxide solution using phenolphthalein as an indicator. The observed first-order rate constants at 71.2 and 80.2° are shown in Table I.

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