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Solvolysis of *syn-endo*-Tricyclo[3,2,1,$0^{2,4}$]oct-6-en-8-yl *p*-Nitrobenzoate

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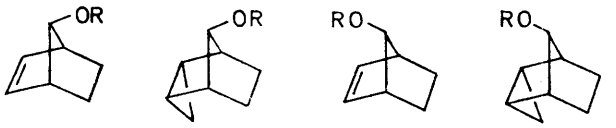
The rates of solvolysis of the title compound in 70% 1,4-dioxan–water were measured at 150, 160, and 170°. At the highest temperature, this material reacts ten times faster than *anti*-norbornen-7-yl *p*-nitrobenzoate. The products of solvolysis in either buffered or unbuffered dioxan–water were examined after six half-lives. Over 90% of the product mixture consists of the alcohol that corresponds to starting material. This result shows that the source of cationic stabilization does not shift during the reaction from the double bond to the cyclopropane ring.

STABILIZATION of developing positive charge at the bridge position † of a norbornyl system may be provided either by a double bond, as in (I),[1] or by a cyclopropane ring, as in (II).[2] The unsaturation must be

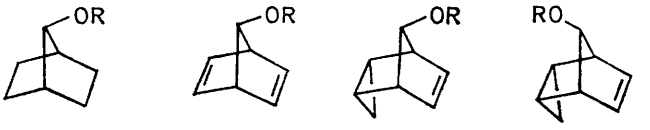
(I) (II)

anti to the leaving group (and *endo* for a cyclopropyl unit) for such participation to occur. Thus, esters (III) and (IV) can produce the ions (I) and (II), respectively, but the *syn*-isomers (V) and (VI) presumably solvolyse without π participation.



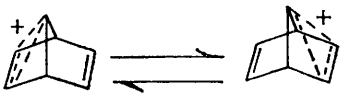
(III) (IV) (V) (VI)

Despite the small rate-retarding inductive effect of the double bond or the cyclopropane ring, the *syn*-compounds (V) and (VI) solvolyse more rapidly than do 7-norbornyl esters (VII).[1c,2c] The presence of a *syn*-double bond in addition to an *anti*-unsaturation, as in (VIII), also causes a rate acceleration by comparison with (III).[1d] N.m.r. studies have demonstrated that the ion (XI) produced from (VIII) is stabilized by only



(VII) (VIII) (IX) (X)

one double bond, although a ' bridge-flipping ' process can reverse the roles of the active and passive double bonds, as in equation (1).[3]



(XI) (XI) (1)

† The bridge position is numbered 7 in compound (I) and 8 in (II).

[1] (*a*) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 1955, **77**, 4183; (*b*) S. Winstein and M. Shatavsky, *J. Amer. Chem. Soc.*, 1956, **78**, 592; (*c*) S. Winstein and E. T. Stafford, *J. Amer. Chem. Soc.*, 1957, **79**, 505; (*d*) S. Winstein and C. Ordronneau, *J. Amer. Chem. Soc.*, 1960, **82**, 2084.

[2] (*a*) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *J. Amer. Chem. Soc.*, 1967, **89**, 1954; (*b*) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, 1967, **89**, 1953; (*c*) J. S. Haywood-Farmer and R. E. Pincock, *J. Amer. Chem. Soc.*, 1969, **91**, 3020.

[3] M. Brookhart, R. K. Lustgarten, and S. Winstein, *J. Amer. Chem. Soc.*, 1967, **89**, 6352.

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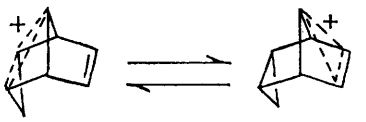
Further information about the function of a *syn* unsaturation would prove useful in understanding these observations. The present study was initiated to clarify the nature of the cations produced at the bridge position of systems that contain two unsaturated units: a double bond and an *endo*-cyclopropane ring. We report the solvolytic properties of the *p*-nitrobenzoate of (X), in which there is an *anti*-double bond and a *syn*-cyclopropane ring. A bridge-flipping process analogous to that in equation (1) interconverts the ions (XII) and (XIII) produced from (IX) and (X), respectively [equation (2)]. This equilibrium differs from the previous one since the ions are not equivalent. Investigation of (X; R = *p*-NO_2·C_6H_4·CO) will therefore give information not only about the effect of a *syn*-

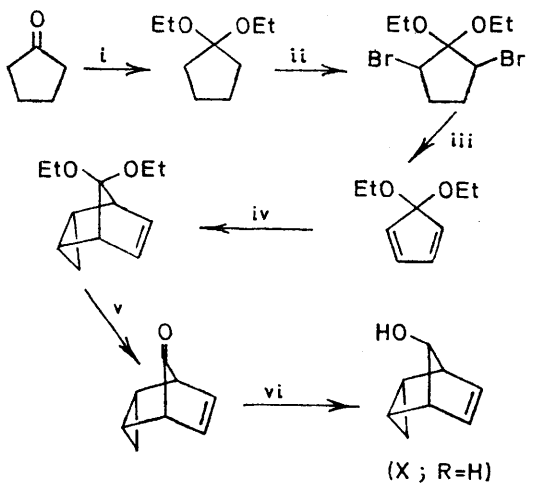


(XII) (XIII) (2)

cyclopropane ring on the solvolysis rate but also about the relative stabilizing abilities of the double bond and cyclopropane ring, both of which are present in the single system.

RESULTS

syn-endo-Tricyclo[3,2,1,$0^{2,4}$]oct-6-en-8-ol was prepared by the method depicted in the Scheme.[2b,4,5] A somewhat different procedure has been used by other workers.[6]



SCHEME

Reagents: i, $HC(OEt)_3$; ii, $C_5H_5NHBr_3$–EtOH; iii, Bu^tOK–Me_2SO; iv, cyclopropene; v, 15% $HClO_4$; vi, $NaBH_4$–MeOH

In our hands, the reduction of *endo*-tricyclo[3,2,1,$0^{2,4}$]oct-6-en-8-one with sodium in liquid ammonia produced the unsaturated *syn* (to the cyclopropane ring) alcohol (X; R = H) and the saturated *anti*-alcohol (IV; R = H). Under the reaction conditions, the double bond of (IX; R = H) apparently was reduced, as observed previously by Franzus and Snyder in similar systems.[7] Reduction of the ketone with sodium borohydride, lithium aluminum hydride, lithium tri-(t-butoxy)aluminum hydride, or aluminum isopropoxide gave almost entirely the *syn*-alcohol (X). Small amounts of (IX; R = H) were observed but not isolated. The highest yields of (X; R = H) were obtained from the borohydride procedure. The crystalline *p*-nitrobenzoate was readily prepared from (X; R = H).

The *endo*-nature of the cyclopropane ring has been established by other workers as the normal result for cyclopropene Diels–Alder reactions.[2,6,8] The *syn*-stereochemistry of the 8-hydroxy-group is proved by the absence of a long-range W-coupling between the 8-proton and the 6,7-alkenic protons.[6,9] The latter protons appear as a very sharp triplet.

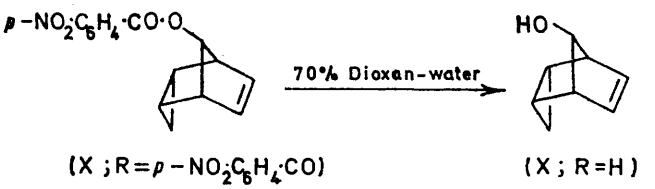
The solvolysis of (X; R = *p*-NO_2·C_6H_4·CO) was carried out in 70% 1,4-dioxan–water, and was followed kinetically by titration with sodium hydroxide in dioxan–water of the *p*-nitrobenzoic acid released. The solvolyses were performed in sealed ampoules at 150, 160, and 170°. The last temperature was chosen to be in common with the published data (k_{170} = 4·89 × 10^{-5} s^{-1}) on the corresponding molecule without a cyclopropane ring (III; R = *p*-NO_2·C_6H_4·CO).[2b] The rate constants for the solvolysis of (X; R = *p*-NO_2·C_6H_4·CO) are presented in Table 1.

TABLE 1

Kinetic data for the solvolysis of *syn-endo*-tricyclo[3,2,1,$0^{2,4}$]oct-6-en-8-yl *p*-nitrobenzoate in 70% 1,4-dioxan–water

Temp. (*T*/°C)	No. of runs	Rate constant/s^{-1}	Half-life/s	Correlation coefficient
150	3	4·54 × 10^{-5}	15,400	0·98
160	4	1·49 × 10^{-4}	4640	0·99
170	2	4·32 × 10^{-4}	1630	0·995

For product studies (X; R = *p*-NO_2·C_6H_4·CO) was allowed to react for six half-lives, at the same concentration as used for the kinetic studies, with 2,6-lutidine (1·5 mol. equiv.) as a buffer.[10] The products were recovered by ether extraction and evaporation. Analysis by v.p.c. on both Carbowax and Silicone columns showed the mixture



(X; R = *p*-$NO_2C_6H_4$·CO) (X; R = H)

to contain one product (*ca.* 90% by peak area), no other being present in more than 3% concentration. This material was recovered by preparative v.p.c. and found to be spectroscopically, and chromatographically, identical to (X; R = H). A similar analysis on the products of

[4] P. E. Eaton and R. A. Hudson, *J. Amer. Chem. Soc.*, 1965, **87**, 2769.
[5] G. L. Closs and K. D. Krantz, *J. Org. Chem.*, 1966, **31**, 638.
[6] S. C. Clarke, K. J. Frayne, and B. L. Johnson, *Tetrahedron*, 1969, **25**, 1265.
[7] B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, 1965, **87**, 3423.
[8] K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, 1965, **30**, 2278.
[9] E. I. Snyder and B. Franzus, *J. Amer. Chem. Soc.*, 1964, **86**, 1166.
[10] W. G. Dauben and J. R. Wiseman, *J. Amer. Chem. Soc.*, 1967, **89**, 3545.

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the unbuffered solvolysis gave an identical product distribution. In contrast, acetolysis of the saturated *syn-endo*-*p*-bromobenzenesulphonate (VI; R = *p*-$BrC_6H_4SO_2$) gives at least ten products.[2c]

DISCUSSION

The relative rate data in Table 2 show that the measured rate of (X; R = *p*-NO_2·C_6H_4·CO) conforms

TABLE 2

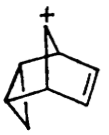
Relative rates for the solvolysis of unsaturated molecules related to the 7-norbornyl system

Molecule	Relative rate [a]	Ref.
(VII)	1	2*c*
(VI)	10	2*b*, *c*
(V)	10^3	1*c*, *d*
(III)	10^9	1*a*, *b*, 2*b*, *c*
(X)	10^{10}	This work
(VIII)	10^{11}	1*d*
(IV)	10^{12}	2*c*

[a] Following the convention of ref. 2*c*, Table III, by which acetolysis rates are related to that of 7-norbornyl *p*-bromobenzenesulphonate; relative rates of *p*-bromobenzenesulphonates and *p*-nitrobenzoates are assumed to be the same.

to a pattern that may be derived from analysis of the various structural components. A double bond that is *anti* to the leaving group conveys an extremely large rate acceleration [(III) relative to (VII)], and the acceleration produced by a similarly positioned cyclopropane ring is slightly larger [compound (VI)]. A *syn*-double bond is also rate enhancing [compound (V)] because it aids in forming an allylic ion,[1c] but a *syn*-cyclopropane ring has only a slight accelerating effect [compound (VI)]. This pattern is similar for doubly unsaturated systems. Thus, a molecule with both a *syn*- and an *anti*-double bond [compound (VIII)] reacts considerably more rapidly than (III). The presently studied molecule (X) has an *anti*-double bond and a *syn*-cyclopropane ring. Consequently, it reacts about an order of magnitude more rapidly than the compound with only the *anti*-double bond, (III), and less rapidly by a similar factor than the compound with both *syn*- and *anti*-double bonds (VIII). The rapid solvolysis rate of (X; R = *p*-NO_2·C_6H_4·CO) is clearly due to an electronic factor (double-bond participation) and not relief of angle strain,[2c] since the product is identical to the starting material.

The first-formed ion in the solvolysis of (X; R = *p*-NO_2·C_6H_4·CO) should be (XIII). The structure of the product indicates that this ion is also product forming, since rear-side attack at the 8-position leads to (X; R = H). Two explanations may be formulated for the absence of (IX; R = H) and other products from the ion (XII). The observed product (X; R = H) is expected to predominate either if the equilibrium of equation (2) favours (XIII) entirely, or if the solvent attacks (XIII) before equilibrium is established. Extended Hückel calculations on ion (XIV) have demonstrated that the primary stabilization derives from interaction with the cyclopropane ring rather than with the double bond.[11] This conclusion is in accord with the relative rates of Table 2, since (IV) reacts more rapidly than (III). These observations suggest that the equilibrium of equation (2) should favour (XII), not (XIII).



(XIV)

If this is the case, the results with (X; R = *p*-NO_2·C_6H_4·CO) can only be explained in terms of a non-equilibrium situation. Bridge flipping must be slow under the conditions of the reaction. The double bond remains the source of cationic stabilization, despite the availability of the more effective *endo*-cyclopropane ring.

EXPERIMENTAL

I.r. spectra were measured on a Beckman IR-5 spectrometer. N.m.r. spectra were obtained with Varian A-60 and T-60 spectrometers. V.p.c. analyses were performed on F and M model 700 and Varian series 1520B instruments. The model 700 instrument was used for preparative work.

1,1-Diethoxycyclopentane was prepared by the action of ethyl orthoformate on cyclopentanone in the presence of acid in 77% yield.[4]

2,5-*Dibromo*-1,1-*diethoxycyclopentane*.—A stirred solution of 1,1-diethoxycyclopentane (30 g, 0·19 mol) in absolute ethanol (375 ml) was cooled in ice–salt to below 5°. Pyridinium perbromide ($C_5H_5NHBr_3$) (121 g, 0·38 mol) was then added and the original red solution became light orange within 0·5 h. White crystals were obtained when the ice–salt-bath was removed. The mixture was then shaken with 10% aqueous sodium carbonate (425 ml) and the resultant mixture was extracted with pentane (5 × 150 ml). The combined pentane extracts were washed with saturated aqueous sodium carbonate (200 ml), 3% hydrochloric acid (200 ml), saturated aqueous sodium carbonate (200 ml), and saturated aqueous sodium chloride (250 ml), dried (1 h) (Na_2SO_4), and then passed through a 1-ft neutral alumina column. Pentane was removed *in vacuo* leaving the dibromide as a colourless, viscous oil in quantitative yield. The material decomposed into a black gum within 24 h at −20°.

5,5-*Diethoxycyclopenta*-1,3-*diene*.—A solution of potassium (43 g, 1·1 mol) in t-butyl alcohol (1 l) was evaporated to dryness on a steam-heated rotary evaporator. To a solution of the potassium t-butoxide obtained, in dimethyl sulphoxide (1 l), freshly prepared 2,5-dibromo-1,1-diethoxycyclopentane (in the amount produced in the previous preparation) in dimethyl sulphoxide (250 ml) was added and the mixture was vigorously stirred for 2 min. The resulting solution was poured onto crushed ice (1 kg) and the product was extracted into cold pentane (6 × 150 ml). The combined pentane extracts were washed with saturated aqueous sodium chloride (2 × 200 ml) and cooled in ice–salt in a 1 l flask equipped with a magnetic stirrer in preparation for cyclopropene addition, which ***must*** follow immediately. The material was never isolated, since it dimerizes in the pure state extremely rapidly.

[11] R. Hoffman, *Tetrahedron Letters*, 1965, 3819.

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Cyclopropene was prepared by the method of Closs and Krantz,[5] in a minimum yield of 14%, as determined by reaction with cyclopentadiene.

8,8-*Diethoxy*-endo-*tricyclo*[3,2,1,$0^{2,4}$]*oct*-6-*ene*.— Cyclopropene was bubbled through the stirred, ice-cooled solution in pentane of 5,5-diethoxy-1,3-cyclopentadiene, made as just described. After 4½ h, the addition was complete, and the solution was dried ($MgSO_4$), and pentane was removed *in vacuo*. The product was distilled *in vacuo* through a micro-Vigreux column to give a clear oil, b.p. 82—83° at 5·5 mmHg (20·0 g, 53% from 1,1-diethoxycyclopentane).

endo-*Tricyclo*[3,2,1,$0^{2,4}$]*oct*-6-*en*-8-*one* was prepared from the diethyl acetal by a procedure analogous to that reported for the dimethyl acetal.[6]

syn-endo-*Tricyclo*[3,2,1,$0^{2,4}$]*oct*-6-*en*-8-*ol* (X; R = H).— The method of Clarke *et al.* was used to prepare this alcohol from the foregoing ketone by reaction with sodium borohydride.[6] The product was purified by preparative v.p.c. (m.p. 61—63°) and had identical spectral properties to those reported.

syn-endo-*Tricyclo*[3,2,1,$0^{2,4}$]*oct*-6-*en*-8-*yl* p-*Nitrobenzoate*. (X; R = *p*-NO_2·C_6H_4·CO).—In dry pyridine (60 ml) was dissolved *p*-nitrobenzoylchloride (6·09 g, 0·0382 mol) recrystallized from ether. The stirred solution was cooled to 0° with an ice-bath and crude *syn-endo*-alcohol (X; R = H) (4·0 g, 0·032 mol) in dry pyridine (40 ml) was added. The resulting solution was stirred at 0° for 4 h, then poured into water (450 ml), and extracted with hexane (6 × 100 ml). The combined hexane extracts were washed with saturated aqueous sodium hydrogen carbonate (150 ml) and water (150 ml) and then dried ($MgSO_4$), and hexane was removed *in vacuo* to leave a yellow oil that crystallized rapidly. The *p*-nitrobenzoate was recrystallized twice from hexane–pentane (1 : 1) to give faintly yellow crystals (5·0 g, 56·5%), m.p. 108—109°; δ 0·46 (sharp m, $-\overline{CH{\cdot}CH_2{\cdot}CH}-$), 1·20 (sharp m, $-\overline{CH{\cdot}CH_2{\cdot}CH}-$), 2·71 (sharp m, partially resolved, bridgehead protons), 4·50 (narrow m, proton α to *p*-nitrobenzoate group), 5·42 (t, alkenic-H), and 7·90 p.p.m. (sharp s, Ar*H*); $\nu_{max.}$ 3120w, 3070w, 2995m, 2860w, 1725s, 1341s, 1103s, 1000s, 842s, 766s, 717s, and 668m cm^{-1}.

Kinetic Procedure.—In 1,4-dioxan–water (70%; 30 ml) compound (X; R = *p*-NO_2·C_6H_4·CO) was dissolved (to give a 0·025M-solution) and 4-ml portions were sealed in seven ampoules. The ampoules were allowed to equilibrate for 10 min in a constant-temperature bath and were then removed in turn after specified time intervals. The reaction was quenched by placing the ampoules in ice–water. The ampoules were opened, and the released *p*-nitrobenzoic acid was titrated with 0·01N-sodium hydroxide in 70% dioxan–water to a bromothymol blue end-point (yellow to blue). The dioxan had been heated under reflux with metallic sodium for 48 h and distilled from the sodium. The solvolysis solvent was prepared by diluting the dioxan with water that had been deionized and distilled through a glass apparatus. The indicator was a 0·4% solution of bromothymol blue in water.

Product Studies.—A 0·025M-solution of the *syn-endo-p*-nitrobenzoate (X; R = *p*-NO_2·C_6H_4·CO) in 70% dioxan–water with or without an equivalent amount of 2,6-lutidine was sealed in a glass tube and placed in an oil bath at 170° for 3 h (six half-lives). The solvolysis was quenched by cooling the tube in ice–water; the tube was opened and poured into saturated aqueous sodium chloride. The products were extracted with ether (×6). The combined ether extracts were washed with saturated aqueous sodium hydrogen carbonate, 1N-hydrochloric acid, and saturated aqueous sodium hydrogen carbonate, and dried ($MgSO_4$). Ether was removed *in vacuo* and the remaining dioxan was evaporated off in the air. The n.m.r. spectrum of the crude product was similar to that of (X; R = H). The products were analysed on both Silicone and Carbowax columns. Product samples were recovered by preparative v.p.c. on a 0·5 in × 10 ft Silicone column.

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