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DECOMPOSITION OF A PHOSPHORYLATED TRIAZOLINE

EVIDENCE FOR THE ABSENCE OF REARRANGEMENT OF THE NORBORNYL SKELETON[1]

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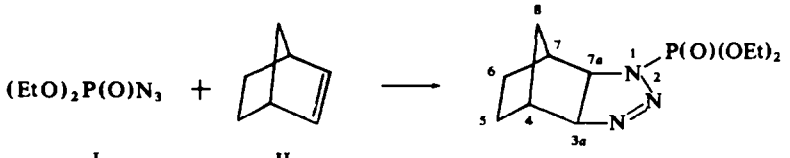
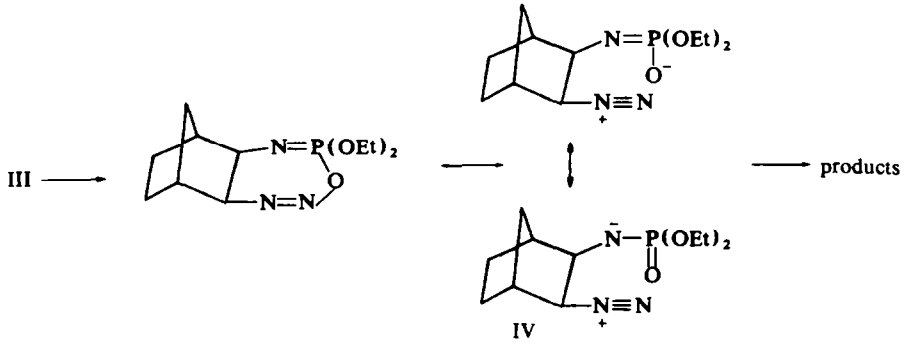
Abstract—Diethyl phosphorazidate (I) and norbornene (II) condense in benzene to give a phosphorylated amidate VI as major product and two minor products, one tentatively identified as an N-phosphorylated eneamine. 5,6-Dideuteronorbornene undergoes the same reaction to give the analogous deuterated products. Hydrolysis of the 5,6-dideuterated phosphorylated amidate XII gave 5,6-dideuteronorcamphor XIV in high yield; XIV was synthesized by deuteration of dehydronorcamphor XVI. On the basis of this evidence and previously obtained kinetic data, the phosphorylated triazoline intermediate formed initially from I and II is postulated to decompose by a highly concerted process in which hydrogen is transferred from C-2 to C-3 in conversion to VI without any major skeletal rearrangement of the norbornyl system.

IN A recent study[3] of the kinetics of the decomposition of the triazoline III, formed from the 1,3-dipolar addition of diethyl phosphorazidate (I) to norbornene (II), it



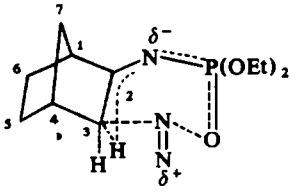
I II III

was proposed that the best fit for the kinetic data was obtained by assuming that the decomposition took place by two consecutive first-order reactions. The increase of the reaction rate constants for the two consecutive first-order reactions with an increase in the dielectric constant of the reaction medium was interpreted to indicate formation of an ionic intermediate which was surmised to be a diazonium betaine IV.



IV

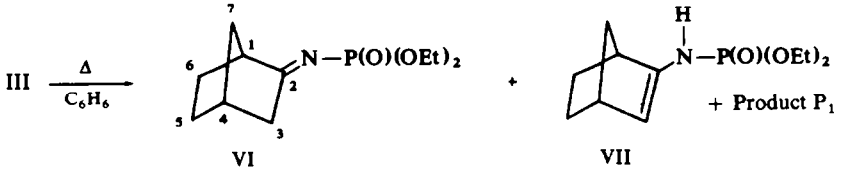
Similar dipolar intermediates have been proposed[4] in the thermal decomposition reactions of triazolines to form aziridines, enamines, ketimines and diazo compounds. The effect of an electron-withdrawing group at N-1 in a similar triazoline in destabilizing the system has been noted.[4d] Considering the ability[5] of the phosphoryl group to stabilize the negative charge on the adjacent atom by resonance delocalization, a 6-membered transition state as shown in V was considered a possibility



V

during the decomposition of III.[3] The large negative entropy of activation ($\Delta S^* = -34$ e.u.) observed for the formation of products from the intermediate IV would be in accord with such a geometrically rigid transition state as V.

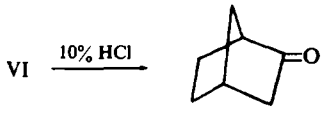
Unanswered from the previous study[3] was whether rearrangement occurred in the norbornyl skeleton during the decomposition. It has now been found that III in boiling benzene over 8·5 hr yielded a product which could be shown by meticulous GLC analysis to be a mixture of three components, in which the compound VI with the longest retention time constituted *a minimum of* 90·6% of the mixture. This preponderant isomer could be isolated pure (purity estimated greater than 97% by NMR as found previously[3]) by fractional distillation and identified to be the phosphorylated amidate VI on the basis of its IR and NMR spectra and chemical degradation.[3] It must be pointed out that on two different GLC columns the ratio of VI:VII + Product P_1 changed as much as 10% as the temperature was raised. Thus it is possible that VI is formed initially as the sole product but a rearrangement occurs on the columns. From the presence, in the crude mixture, of bands at 3448 and 3226 cm^{-1} in the IR spectrum (film) and a triplet at 360 c/s, ascribable to an



VI VII

olefinic proton in the NMR spectrum, the presence of the enamine VII[6] (<5%) was tentatively inferred (when the mixture was treated with D_2O, a small peak for HDO appeared). No insight into the nature of the third component (Product P_1 <5%) could be obtained. All attempts to separate the components of the mixture proved unsuccessful. On prolonged heating of the mixture, as is necessary in precise fractionation, decomposition resulted. Use of preparative TLC and GLC for effecting this separation led to the same result. Column chromatography over alumina resulted in partial decomposition and no complete separation. In the light of these

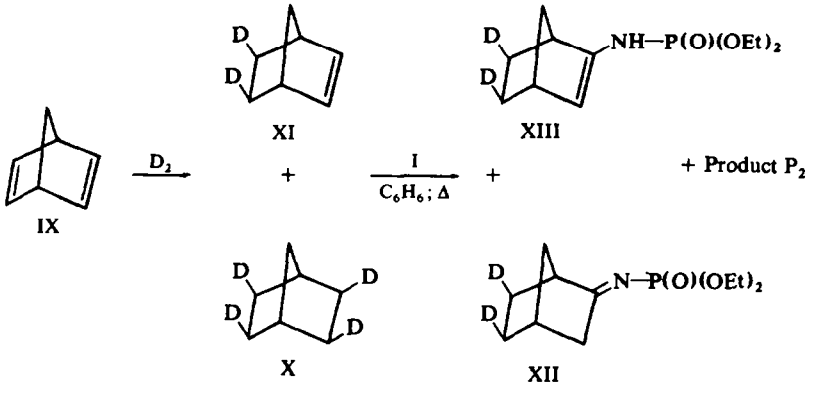
results further investigation was conducted on the amidate VI which had been purified by distillation and in which the proportion of the other two components constituted only a very small percentage of the mixture. Treatment of the amidate VI with 10% hydrochloric acid for 1 hr at room temperature gave norcamphor (VIII) (in a yield of 71%) which was purified by sublimation. The IR and NMR



VIII

spectra were identical with those of an authentic specimen and GLC analysis showed a single peak. In the earlier work[3] in which norcamphor was isolated as the corresponding 2,4-dinitrophenylhydrazone, the yield was 85%; the reduced yield in this case can be attributed to the high volatility of norcamphor.

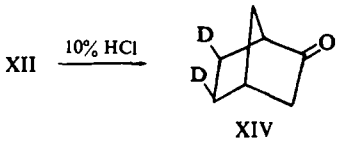
The same series of reactions were now carried out on 3,6-dideuteronorbornene (XI) prepared by deuteration of norbornadiene in benzene or ether over 5% Pd/C as described in the literature.[7] The course of the reaction was followed by GLC analysis, and it was found that absorption of 1·5 molar equivalent of deuterium was necessary to avoid the presence of residual norbornadiene (IX). The mixture of 3,6-dideuteronorbornene (XI) and 2,3,5,6-tetradeuteronorbornane (X) thus obtained was treated (without further separation) with diethyl phosphorazidate (I) in boiling benzene for



55 hr at which time the evolution of N_2 had ceased. From GLC analysis, the crude mixture was found to consist of the deuterated analogs of the three compounds and unreacted X. The distilled material consisted mainly of XII and showed peaks in its spectrum (film) at 2173 (C—D), 1644 (C=N) and 1250 cm^{-1} (P → O). Very small absorption at 3448 cm^{-1} (N—H) suggested the presence of the enamine XIII. The NMR spectrum of distilled XII was comparable with that of the nondeuterated analog VI[3] except for the following differences. The area of the peaks at high field (60–100 c/s) was reduced by a factor equivalent to two protons and the widths at half-height (W_H) of the peaks at 153 and 178 c/s were reduced by 2 and 3·5 c/s, respectively. This supports the earlier assignment[3] that the signals originate from the

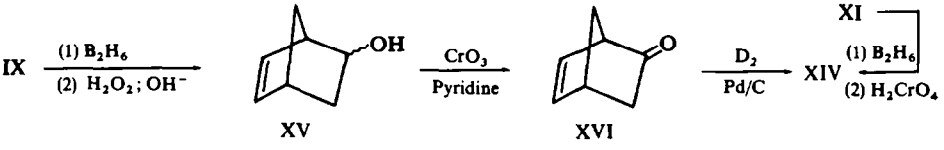
C-1 and C-4 bridgehead protons in VI. The two-proton multiplet in the region 130–150 c/s could be ascribed to the C-3 protons (*vide infra*).

That the deuterium atoms in XII were located at C-5 and C-6 and that they were *exo*-oriented was evident when, on acidic hydrolysis, the amidate XII gave 3,6-dideuteronorcamphor (XIV) in good yield. Sublimation of this material gave a pure



XIV

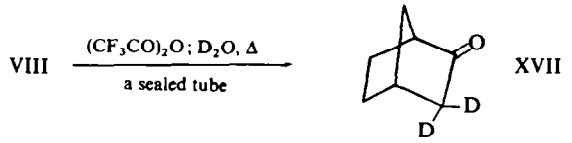
sample. Proof of the identity of the ketone XIV was furnished by an alternative synthesis from norbornadiene (IX). Monohydroboration of IX followed by oxidation[8] yielded dehydronorbornanol (XV), which was treated in crude condition with chromium trioxide and pyridine as described elsewhere[9] to give dehydronorcamphor (XVI). Deuteration of XVI in ether over 10% Pd/C, followed by chromatography



XV XVI

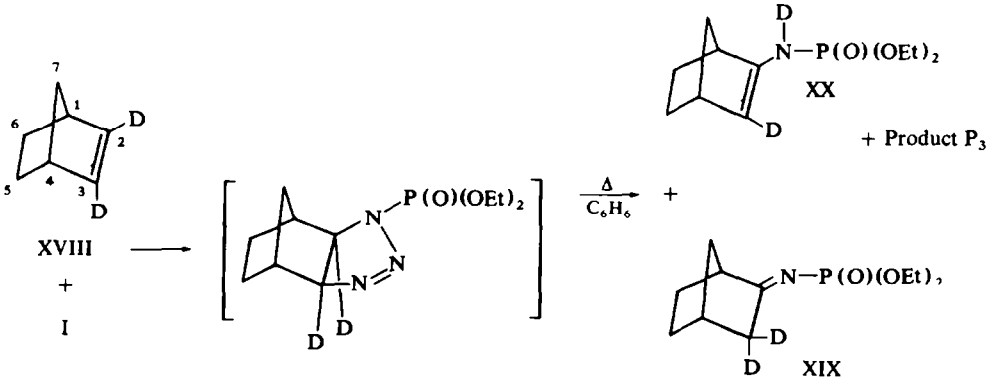
over alumina, gave a pure sample of 5-*exo*,6-*exo*-dideuteronorcamphor (XIV) whose IR and NMR spectra were identical in all respects with those of the sample obtained from the amidate XII. Ketone XIV was also synthesized from 3,6-dideuteronorbornene (XI) by another sequence of reactions. The alkene XI was hydroborated,[10] and the resulting organoborane was oxidized directly with chromic acid.[11] Chromatography of the product over alumina gave a liquid by-product (from petroleum ether fractions) and a solid product (from petroleum ether–ether fractions). The latter, after sublimation, was characterized as 3,6-dideuteronorcamphor (XIV) on the basis of comparison of its physical properties with those of the samples obtained previously. This observation is contrary to the recorded[12] rearrangements during the chromic acid oxidation of organoboranes of certain norbornyl systems.[13] Confirmation of the structure and stereochemistry of the ketone XIV is based on the well-known and proved[7,14] *exo-cis* addition of deuterium or hydrogen during catalytic reduction of double bonds in the bicyclo[2.2.1]heptene system. The IR and NMR spectra further supported this point of view. In the IR spectrum of XIV, the C—D stretching frequency occurred as a broad peak at 2183 cm^{-1}, the carbonyl frequency being at 1751 cm^{-1}. Characteristic differences in the finger-print region from that of norcamphor (VIII) were also observed. In the NMR spectrum of XIV the *exo*-orientation of the deuterium atoms at C-5 and C-6 was apparent by the occurrence of a broad singlet (2H) at 80 c/s assignable to the *endo*-protons at C-5 and C-6. Had these protons been *exo*-, they would be expected to give rise to a broad multiplet because of coupling with the adjacent bridgehead protons at C-1 and C-4. The broad multiplet in the region 95–125 c/s (2H) was attributed to the C-3 protons since the

major peaks in this region disappeared (loss of 2 protons) in the NMR spectrum of 3,3-dideuteronorcamphor (XVII), prepared by a reported procedure.[15] A similar observation has been made by Corey *et al.*[16] There were two peaks in the downfield



region at 145 c/s (1H, broad multiplet, W_H = 7·5 c/s) and at 135 c/s (1H, broad singlet, W_H = 3·75 c/s) in the NMR spectrum of XIV. Though the chemical shifts of these two peaks were the same in the spectrum of norcamphor (VIII), it was noted that, in the latter case, the W_H = 5·25 c/s (1·5 c/s more than with XIV) for the *peak at* 135 c/s. The W_H of the peak at 145 c/s was unaffected. *This observation is very significant for making correct assignments for these peaks.* To date, these signals have been assigned[16, 17] to the bridgehead protons at C-1 and C-4. Pointedly, because of the diminution in the intensity of the peak at higher field at 7·62 γ[16] (142 c/s as found by others;[16] the proton on this carbon occurred at 135 c/s in our work) with partial deuteration at C-1 in norcamphor (VIII), this peak has been assigned to the proton at C-1. The reduction in W_H of this peak in the spectrum of XIV, where the C-6 *exo* H has been replaced by D, is in full agreement with this assignment. At the same time, the insensitivity of the *peak at* 145 c/s to *exo*-D substitution at C-5 makes the assignment of this peak to the proton at C-4 dubious. Examination of the spectrum of 3,3-dideuteronorcamphor (XVII) permits a tentative assignment for the signal at 145 c/s. In the spectrum of XVII, the W_H of the peak at 135 c/s was unaffected, whereas the *peak at* 145 c/s had W_H = 6·0 c/s which is 1·5 c/s less than in the case of norcamphor (VIII). Other than the proton at C-4, the only remaining unassigned proton which reasonably could be coupled to the C-3 protons in norcamphor (VIII) would be the *anti*-C-7 proton by a long-range coupling through the favoured W arrangement of the bonds.[18] This anomalous difference in the chemical shifts of the C-7 methylene protons has an analogy in the similar situation observed in the case of norbornene and benzonorbornene[19] and is to be traced most probably to the diamagnetic anisotropic effect of the carbonyl group.

Treatment of 2,3-dideuteronorbornene* (XVIII) with diethyl phosphorazidate (I)

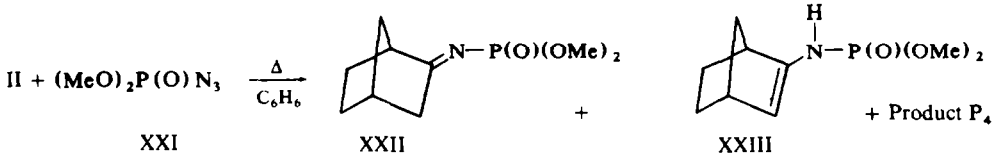


* We are thankful to Dr. John Stille for the gift of this compound.

yielded the corresponding triazoline which, without isolation, was decomposed in boiling benzene and gave a mixture (as analyzed by GLC) which consisted of the amidate XIX, the enamine XX (tentatively assigned) and one unknown very minor component. In the IR spectrum (film) of the reaction mixture there were peaks at 2222, 2164 and 2053 cm^{-1} (N—D and C—D), 1672 cm^{-1} (C=N) and 1257 cm^{-1} (P → O).

The NMR spectrum of the distilled compound XIX containing a trace amount of XX was comparable to that of the nondeuterated analog VI except for the fact that the intensity of the multiplet in the region 130–150 c/s was reduced by 70% indicating that these signals arise from the C-3 protons as surmised earlier. Thus, this reaction mixture was essentially identical to that previously obtained from the nondeuterated II and I.

The Me analogs XXII and XXIII of compounds VI and VII, respectively, were also prepared by treating norbornene (II) with dimethyl phosphorazidate (XXI) in

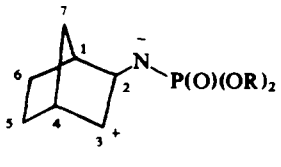


XXI XXII XXIII

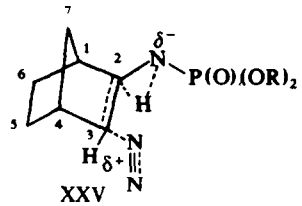
boiling benzene. The crude product showed absorption in the IR (film) at 3626 (N—H), 1666 (C=N) and 1265 cm^{-1} (P → O). In the NMR spectrum ($CDCl_3$) there were signals at 222 (6H, doublet, O—Me), 180 (1H, m*) and 158 c/s (1H, m) attributed to the bridgehead protons; 140 c/s (2H, m, C-3 protons); and in the region 60–127 c/s (6H, broad m) ascribed to the protons at C-5, C-6 and C-7. The NMR spectrum of a distilled sample indicated that the compound was mainly the amidate XXII with only negligible amounts of other products. This product XXII proved to be less stable than the corresponding ethyl derivative, however, and some decomposition occurred in less than one hour even when the sample was stored near 0°. Consequently, no further work was done with the system but the data accumulated strongly suggests the reaction mixture is very similar to that obtained from I and II.

Isolation of 3,6-*dideuteronorcamphor* (XIV) *by the hydrolysis of the amidate* XII *in good yield offers unambiguous proof of the absence of large scale rearrangement of the norbornyl skeleton during the decomposition of the triazoline* III. In view of the well known[20] tendency of norbornyl cations to undergo rearrangements by participation of the C-4—C-5 bond and scrambling of the deuterium, the conclusion appears untenable that a *free* ambident ion of the type XXIV is formed in this reaction. Also the breaking of the C-3—N bond should occur by a process in which concurrent bond formation to this carbon atom takes place with hydride or a new π bond is generated with C-2. In other words the C-3 carbon atom may not attain full sp^2 hybridization in the transition state, but the degree to which this hybridization is approached is not known. Decomposition of IV could be viewed as proceeding

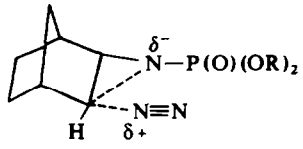
* m = multiplet.



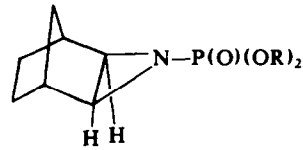
XXIV



XXV



XXVI



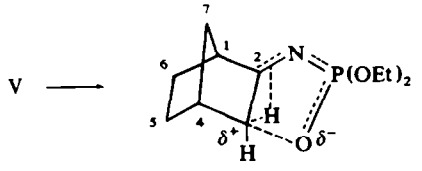
XXVII

through any of the transition states V, XXV or XXVI which could be expected to lead to the amidate VI, the enamine VII or the aziridine XXVII, respectively (and also be supported by the kinetic data), as the initial product. We have no direct evidence for aziridine formation (Product P_1 $<5\%$) in our experiments but others have found aziridines in reaction of certain azides with norbornene.[4b,d,e,f] It is possible that an equilibrium exists between all three products by appropriately conceived hydrogen shifts in view of the change in ratio of VI: VII + Product P_1 with temperature change on the GLC column (Product P_1 could be the aziridine XXVII where R = Et). To state it explicitly, it is felt that the presence of a resonance-stabilized internal nucleophile in the transition state from IV to product precludes to a large extent the rearrangement of the norbornyl skeleton.* The aziridine XXVII has just been reported in the literature.[31]

Transition state V is open to objection in that it implies a 2,3-*endo,endo* hydride migration, a process not known to occur in the norbornyl system.[20,22,23] The preference for 2,3-*exo,exo* shift over 3,2-*endo,endo* shift has been demonstrated in the pinacol rearrangement of 2-substituted norbornane-2,3-*cis,exo* diols, a reaction whose mechanism has been studied in great detail.[24] The *exo*-shift seems[25d] to be preferred by at least a factor of 100. However, 2,3-*endo,endo* hydride migration has recently been shown[26] to occur in the bornyl system during the pinacol rearrangement of 3-*endo*-phenyl-2,3-*exo,cis*-bornanediol. Nevertheless, the steric and torsional factors in the norbornyl system should differ from those in the bornyl system. Transition state XXV involves abstraction of the proton at C-2 by the negatively charged nitrogen atom with simultaneous formation of a double bond between C-2 and C-3 atoms. Transition state XXVI which involves C-3—N bond-formation with simultaneous rupture of the C-3—N_2 bond is related to a possible intermediate tentatively suggested for the formation of the corresponding aziridine from reaction of II with benzenesulfonyl azide.[27] Consequently, because of the high negative

* A detailed GLC analysis of the reaction mixture of 2,3-dideuteronorbornene and benzenesulfonyl azide was not included in a published report.[21] The corresponding sulfonylated aziridine was isolated in a yield of 53%. The extent of skeletal rearrangement cannot be evaluated (no GLC analysis of the deuterated mixture) but could be minimal and thus be parallel to our results.[21b].

entropy found for conversion of IV to VI[3] and the lack of much skeletal rearrangement as evidenced by the isolation of XIV (in high yield) from reaction of XI with I, we are forced to conclude the transition state is highly concerted. Moreover, isolation of XIX from reaction of XVIII with I lends credence to a 2,3-*endo–endo* hydride migration. It must be recalled also that NMR analysis of the reaction mixture (this was before analysis by GLC) indicated VI as the major product and addition of D_2O caused the appearance of only a very small DHO peak which is derived from VII. Protons in Product P_1 are not discernible by NMR analysis at 60 Mc partly because of very low concentration and probably masking. On the basis of all of this evidence, we are therefore suggesting that VI is probably formed initially from IV although we cannot rule out initial formation of VII (perhaps via transition state XXV) which rearranged *very rapidly* to VI. If VI is formed directly through a transition state such as approximated by V, the possibility of stabilization of an incipient cation *via* the P=O as illustrated in XXIX is not unreasonable in view of the high entropy value of



XXIX

−34 e.u. found for the second step of the reaction[3] but cannot adequately be evaluated. Thus, the ease of transfer of a hydride group from C-2 to C-3 may also well depend upon this factor as well as the degree of sp^2 character at C-3. If VII (or Product P_1) is the first product from IV, *via* perhaps XXV, *a thermal catalyzed hydrogen shift to give* VI *must be facile* although we know of no simple analogy for this rearrangement. Pseudo-Wittig reagents of the type $R\tilde{N}—\overset{O}{\overset{\|}{P}}(OR')_2 \leftrightarrow RN=\overset{O^-}{\overset{|}{P}}(OR')_2$ are known,[5] and the resonance delocalization in the hybrid approximate is reminiscent of that shown.

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were recorded with a Beckman IR-5A instrument. NMR spectra were run on a Varian A-60 spectrometer. The spectra were taken in CCl_4 unless otherwise stated. Alumina (Fisher Scientific Co.) was activated at 250° for 10 hr before use.

Diethyl 2-norbornylidenephosphoramidate (VI)

A mixture of II (13·2 g, 0·14 mole) and I (10·0 g, 0·056 mole) was heated at 40–45° for 50 hr and the product was decomposed by heating to reflux in benzene (50 ml) for 9 hr. The solvent was removed and the residue was distilled to obtain VI as a colorless oil (10·53 g, 77%), b.p. 117–118° (0·3 mm), $n_D^{23°}$ 1·4788; IR and NMR spectra were identical with those of the sample reported earlier.[3]

Hydrolysis of the phosphoramidate (VI). The phosphoramidate VI was stirred with 10% HCl (10 ml) for 1 hr at room temp. The mixture was diluted with water (25 ml), neutralized ($NaHCO_3$ aq), and extracted with ether. The combined organic extracts were washed with water and brine and dried (Na_2SO_4). The solvent was carefully removed by fractionation first at atm press and later under reduced press (100 mm) to obtain VIII (0·32 g, 71·3%). Sublimation gave the pure sample, m.p. 88–9·1°, whose spectral features

were identical with those of an authentic sample of norcamphor which had been purified through the semicarbazone.

Diethyl 2-(5,6-exo,exo-*dideuteronorbornylidene*)*phosphoramidate* (XII)

A benzene soln of a mixture of XI and X, prepared by the deuteration[7] (1·5 molar equiv) of IX (10·0 g) in the same solvent, was heated at reflux with I (2·1 g) for 55 hr at which time the evolution of N_2 ceased. The solvent was removed and the residue was distilled to obtain *diethyl* 2-(5,6-exo,exo-*dideuteronorbornylidene*)*phosphoramidate* (XII) as a colorless oil (2·55 g, 88%), b.p. 109–112° (0·1 mm); the material contained small amounts of the other two components as shown by GLC [Columns: SE-30 on Chromosorb W, A–W, DMCS, 60·80 mesh and 6% Silicone Rubber on Chromosorb G, A–W, DMCS, 80·100 mesh].

Hydrolysis of diethyl 2-(5,6-exo,exo-*dideuteronorbornylidene*)*phosphoramidate* (XII). The hydrolysis was carried out with XII (1·0 g) as described above and gave XIV (0·34 g, 75%; this is actual compound obtained in pure form by GLC analysis. The actual crude product was isolated in quantitative yield but the extreme volatility of XIV makes for difficulty in preventing losses of material). Sublimation gave a pure sample, m.p. 92–94°.

Synthesis of 5,6-exo,exo-*dideuteronorcamphor* (XIV)

(a) *From norbornadiene* (IX). This IX (18·4 g, 200 mmoles) was converted into XV following the general procedure described[8] using the following reagents: lithium borohydride (0·54 g, 25 mmoles), BF_3-etherate (4·60 g, 33 mmoles), ether (35 ml), NaOH (1·26 g in 10·5 ml water) and 30% H_2O_2 (10·5 ml). The crude product (13·0 g), consisting of a mixture of XV and unreacted starting material IX (ratio 1:2:·75), was oxidized as described using CrO_3 (26·0 g) and pyridine (360 ml). The crude residue obtained was distilled to give XVI as a colorless oil (3·65 5, 16·8% based on IX), b.p. 50–54° (20 mm), $n_D^{26°}$ 1·4828; IR: 1745 and 1694 cm^{-1} (C=O); NMR (CCl_4): 388 (1H, C-6—H, d* of doublets J = 5·5 and 3 c/s), 361·5 (1H, C-5—H, d of doublets with finer splitting), 188 and 170 (1H each, C-1 and C-4 protons, m), 120 (2H, 3-3—protons, m) and 106 c/s (2H, C-7 protons, m). Ketone XVI (3·65 g) in ether (100 ml) was stirred in the presence of 10% Pd/C (0·35 g) in an atmosphere of deuterium for 1·25 hr. The soln was filtered and concentrated slowly through a Vigreux column. Removal of the last traces of solvent at 100 mm gave a crude residue (3·5 g) which was chromatographed over alumina to yield XIV as a white solid (1·92 g) sublimation of which yielded the pure sample (1·52 g), m.p. 93–95°; the IR and NMR spectra were identical with those of the sample obtained from the hydrolysis of the deuterated XII.

(b) *From* 5,6-exo,exo-*dideuteronorbornene* (XI). Compound XI (6·6 g, 68 mmoles in 45 ml ether) was hydroborated[10] and oxidized[11] as described for norbornene using the following materials: $LiBH_4$ (0·42 g), BF_3–etherate (3·64 g in 20 ml ether), sodium dichromate dihydrate (14·0 g), conc H_2SO_4 (10·5 ml) and water (60 ml). The crude product (5·4 g) was chromatographed over alumina and gave a colorless liquid side-product (1·55 g from pet ether fractions) and XIV as a white solid (2·0 g from a 2:1 mixture of pet ether and ether). Slow sublimation gave a sample (1·62 g), m.p. 90–93°, whose spectral features were identical with the sample obtained by the other route.

3,3-*Dideuteronorcamphor* (XVII). Norcamphor VIII (6·2 g) was treated twice with D_2O (19·6 g) and trifluoroacetic anhydride (16·0 g) as described[15] to get the crude product (5·5 g) which was fractionally sublimed to give pure XVII (2·59 g), m.p. 92·5–94·5°, IR: 2212, 2169 and 2123 cm^{-1} (C—D), and 1742 cm^{-1} (C=O).

Diethyl 2-(3,3-*dideuteronorbornylidene*)*phosphoramidate* (XIX)

Compound XVIII[28] (0·152 g) was treated with I (0·115 g), and the product was decomposed as described above and gave a colorless oil (157 mg). Shortpath distillation of the oil at 90–100° (0·05 mm) gave *diethyl* 2-(3,3-*dideuteronorbornylidene*)*phosphoramidate* (XIX) as a colorless oil (0·092 g, 58·5%) contaminated with trace amounts of the other two components as indicated by GLC analysis. NMR analysis supports the structure XIX as described in the text. It was found that XVII suffered exchange of deuterium under conditions of hydrolysis used with XIV. Thus, hydrolysis of XIX was not of practical significance.

Dimethyl 2-*norbornylidenephosphoramidate* (XXII)

(a) Dimethyl phosphorazidate XXI. Chlorination of trimethyl phosphite (153·0 g, 1·24 moles) was carried out following the procedure of McCombie *et al.*[30] to obtain dimethyl phosphorochloridate as a

* d = doublet.

colorless liquid (120·0 g, 67·5%); $n_D^{22.5°}$ 1·4112. Following the available procedure[27] for the preparation of phosphorazidates, dimethyl phosphorchloridate (50·0 g, 0·34 mole) was treated with sodium azide (66·3 g, 1·02 mole) in dry acetone (500 ml). The crude product on distillation gave *dimethyl phosphorazidate* (XXI) as a colorless liquid (22·4 g, 43%), b.p. 60–63° (2 mm), $n_D^{26°}$ 1·4248; IR (film: 3367, 2500, 2155 (—N_3) and 1625 (P → O), lit.[30] b.p. 79·5–81°/10 mm, n_D^{20} 1·4276.

(b) *Treatment with norbornene* (II). Compound XXI (1·00 g, 6·62 mmoles) and II (2·00 g, 20·2 mmoles) in benzene (100 ml) were heated at reflux for 55 hr. Removal of the solvent gave a crude material (1·20 g) which on distillation yielded *dimethyl 2-norbeonylidenephosphoramidate* (XXII) as a colorless oil (0·87 g, 73%), b.p. 97–102° (0·05 mm), $n_D^{22.5°}$ 1·4818. This compound is less stable than the corresponding Et derivative as evidenced by a change in color of a sample upon standing for a short time. The structure of XXII rests on the NMR data since decomposition was sufficiently rapid to prevent good elemental analysis.

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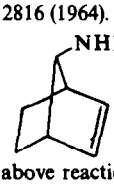
[6] A referee has commented that the bridge compound VII', 

cannot be wholly eliminated. We have found that the crude mixture from the above reaction is hydrolyzed to norcamphor in yield greater than 97% (by GLC). Of course VI and VII are logical precursors of VIII but Product P_1 or VII' cannot be evaluated in this respect.

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