concentrations had an important effect. This could be attributed to the known reaction of hydrogen sulfide with the metals in the reactor walls. When a glass reactor was used, the effect of hydrogen sulfide on the sulfur–bibenzyl reaction was nearly linear.

The ultimate success of using sulfur and H_2S to cleave bibenzyl will depend upon controlling the formation of high molecular weight products. These materials have sulfur incorporated into their structures. The two-step reactions in Table IV show that desulfurization of 2-PBT and 4-PT is readily accomplished but recovery of higher molecular weight products is more difficult. Inclusion of hydrogen in a high-sulfur reaction, Table IV, demonstrates that improving the mass recovery is possible while maintaining high reactivity in the bibenzyl–sulfur system to yield toluene.

In conclusion, elemental sulfur is shown to be very reactive with bibenzyl at conditions that would be considered as relatively low coal liquefaction temperatures and short reaction times.

Acknowledgment. We are grateful for the financial support via a Mining and Mineral Resources Research Fellowship (R.D.H.), a Fellowship from the University of North Dakota Energy Center (R.D.H.), and a contract from the Department of Energy. We thank David Miller for providing GLC/MS data and Art Ruud for the gas analyses.

Stereochemistry of P–N Bond Cleavage. First Crystal and Structural Assignment in Cyclic Phosphoramidofluoridates†

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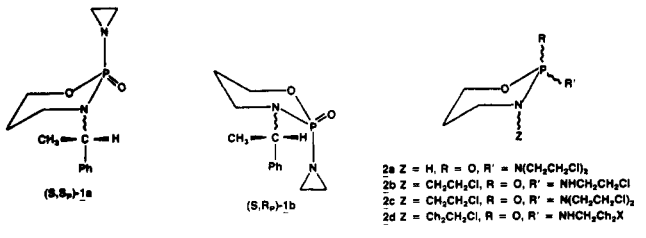
Diastereomers of 2-(*N*-ethyleneimino)-2-oxo-3-(α-methylbenzyl)-1,3,2-oxazaphosphorinane have been found to react with poly(hydrogen fluoride–pyridine). Displacement of the ethyleneimino ligand by the fluoride ion is fully stereospecific and occurs with inversion of configuration at the P atom. This is proved by X-ray crystallographic examination of the product resulting from 2(*S*)-(ethyleneimino)-2-oxo-3-[(*S*)-α-methylbenzyl]-1,3,2-oxazaphosphorinane. In this product the phosphorinane N atom is nearly planar and, thus, is equatorially substituted.

Diastereomers of 2-(*N*-ethyleneimino)-2-oxo-3-(α-methylbenzyl)-1,3,2-oxazaphosphorinane (**1**) have proven to be valuable intermediates in the synthesis of enantiomeric forms of alkylating anticancer drugs such as cyclophosphamide and its congeners (**2**).[1] The abolute configuration at the P atom in diastereomers of **1** was unambigously assigned by X-ray crystallographic determination of the absolute configuration in both enantiomers of cyclophosphamide (**2a**),[2] which was derived from **1** by stereochemically well-defined pathways: opening of the aziridinyl ring by means of HCl, chloroacetylation at the exocyclic nitrogen atom, and sequential reduction of the carbonyl function with diborane followed by hydrogenolytic cleavage of the α-methylbenzyl/carbon–endocyclic nitrogen bond. All of the steps occur without cleavage of any bond directly attached to the stereogenic phosphorus atom.



Since alkylating and chemotherapeutic properties of cyclophosphamide congeners may differ from the parent compound **2a** if the β-halo alkyl function attached to the nitrogen atom is varied, we investigated the stereospecific synthesis of compounds **2d**, X = Br, I, SO_3CF_3, F. We present here the stereochemical results of the reaction of **1** with poly(hydrogen fluoride–pyridine) (**3**).

Discussion

In contrast to the reaction of **1** with hydrogen bromide, which leads to opening of the aziridinyl ring and formation of the corresponding (β-bromoethyl)amido derivative **2d**, X = Br,[3] treatment of (S,S_p)-**1** with **3** under strictly anhydrous conditions leads to the cleavage of the phosphorus–exoxyclic nitrogen bond and formation of 2-fluoro-2-oxo-3-(α-methylbenzyl)-1,3,2-oxazaphosphorinane (**4**). This observation is not unprecedented: Skrowaczewska and Mastalerz in 1955 reported splitting of the P–N bond by hydrogen halides[4] and Greenghalgh and Blanchfield in 1966 demonstrated that the reaction of dialkyl phosphoramidates with hydrogen fluoride gives dialkyl phosphorofluoridates.[5] However, compounds such as isophosph-

† This work is dedicated to Prof. Jan Michalski on the occasion of his 65th birthday.

‡ Polish Academy of Sciences.

§ National Heart, Lung, and Blood Institute.

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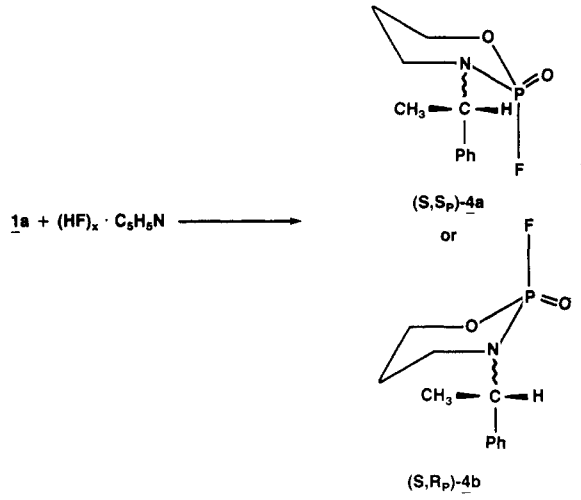
amide (**2b**), 2-(*N*-phenylamino)-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane and its *N*-cyclohexyl analogue, 2-(*N*-methyl-*N*-phenylamino)-2-oxo-4-methyl-1,3,2-dioxaphosphoriane, and *O*-methyl *O*-benzyl *N*-(α-methylbenzyl)phosphoramidate, under the conditions of reaction of **1** with **3**, were recovered unchanged.[3] It should also be emphasized that reaction of **1** with **3** is chemoselective; only the exocyclic P–N bond is cleaved and the endocyclic one remains intact.

^{31}P NMR studies have shown that diastereomerically pure **1a**, when treated with **3** gives a single compound **4a**, $^{31}P\delta$–3.2, $^{1}J_{PF}$ = 996 Hz (in benzene solution). Under identical conditions the mixture of diastereomers **1a**/**1b** (79:21) was converted to the mixture of diastereomers **4a**/**4b** in the identical ratio 79:21; **4b**: $^{31}P\delta$–2.0, $^{1}J_{PF}$ = 1001 Hz (benzene), thus proving the stereospecificity of the reaction. Although it is reasonable to assume that acid-catalyzed P–N bond cleavage occurs with inversion of configuration at phosphorus, as is known to be the case in solvolysis of optically active phosphoramidates,[6] a direct proof of the stereochemistry of this reaction is necessary. Chemical correlation between **4a** and other 1,3,2-oxazaphosphorinanes of known absolute configuration at phosphorus are inconclusive. For example, reaction of (R_p)-2-chloro-2-oxo-3-[(*R*)-α-methylbenzyl]-1,3,2-oxazaphosphorinane with NH_4F, LiF, or KF, even in the presence of a crown ether (18-crown-6), in either boiling benzene or acetonitrile, did not lead to the expected compound **4**. However, diastereomer **4a**, when crystallized from benzene–*n*-hexane (1:3) solution, gave well-defined crystals which were used for X-ray crystallographic studies.



The bond lengths, angles, and absolute configuration are as shown in Figure 1. The phenyl ring does not deviate significantly from planarity and makes an angle of 65.0° with the mean plane of the oxazaphosphorinanyl ring. It should be noted that the F atom is axial and that the two stereogenic atoms, P and C(6), are both *S*. The oxazaphosphorinanyl ring has a chair conformation although the torsion angles are somewhat smaller than in cyclohexane. The largest deviations are shown by the C–O–P–N and C–N–P–O torsion angles which are –42.8 and 40.0°, respectively. An accompanying widening of the angles at the endocyclic O and N atoms is apparent and the N substitution is equatorial but the N atom is nearly planar. There do not appear to be any reported crystal structures of the –O–P(O,F)–N– moiety with which to make comparisons, but the unit may be described as tetrahedral with angular

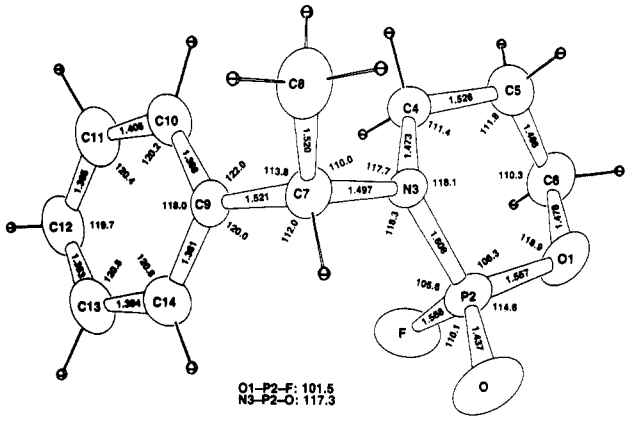


Figure 1. The crystal conformation and molecular dimensions of **4a**. Standard deviations of heavier atom bond angles are ≤0.2° at the P atom and ≤0.6° elsewhere. The standard deviations of bond lengths are ≤0.004 Å at the P atom and ≤0.009 Å elsewhere.

deviations of as much as 8° from regularity. The bond lengths suggest that the exocyclic P–O bond is a double bond and that the other bonds are single. There are similarities to the dioxaphosphorinane structure reported by Clardy et al.,[7] especially in the widening of the ring bond angles adjacent to the P atom, but the incorporation of an endocyclic N atom instead of an O atom has produced significant differences. The P–N bond, while in the usual range of 1.58–1.63 Å, is considerably longer than the corresponding P–O bond which, in turn, is longer than the P–O bonds in the dioxaphosphorinane; the P–F bond is also longer but the exocyclic P–O bond is similar. There are no very short nonbonded contacts although some F···H and F···O distances are 0.1 Å less than the van der Waals distances given by Bondi.[8]

Thus, it is clearly proven that the conversion 1 → 4 under the action of **3** occurs with inversion of configuration at phosphorus. Assuming that the first step involves the protonation of the exocyclic aziridinyl nitrogen atom, the most probable structure for the transition-state or short-lived intermediate **5a** involves a trigonal bipyramid with a six-membered ring spanning equatorial–equatorial positions, and colinear disposition of both the aziridinyl group and the fluorine atom in apical positions. Its collapse leads to product **4** with inversion of configuration at the P atom. However, no spectroscopic evidence (^{31}P NMR monitoring of the reaction dynamics) was obtained to support the presence of pentacovalent intermediates. Any other assumption, such as an equatorial–apical position of the six-membered ring, involves several steps of pseudorotational isomerizations and seems to be less probable. The possibility that the phosphoryl oxygen atom serves as a site of protonation must also be considered. Colinear attack of fluoride ion opposite to aziridinyl nitrogen atom would also lead to inversion. Alternatively, fluoride ion attack from the direction colinear with the endocyclic oxygen atom would lead to an intermediate with equatorial–apical disposition of attacking and leaving groups (**5b**), and the formation of a product **4** with inverted configuration with respect to the substrate would require involvment of pseudorotary pathways.[9,10] In the light of the findings of Gerlt et al., concerning the stereochemistry of

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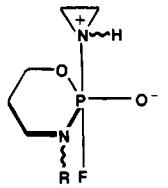
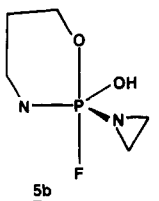
hydrolysis of cyclic diesters,[11] it is possible that pseudorotational processes are not necessary in nucleophilic substitutions at a phosphorus atom that is not incorporated into a small-ring system ($n < 5$).



5a



5b

Cleavage of the phosphorus–exocyclic N–aziridinyl bond is sterospecific, as demonstrated above in the reaction of **1a/1b** with **3** leading to **4a/4b** in the same ratio of diastereomers as that in the starting material. Interestingly, no traces of products resulting from the opening of the oxazaphosphorinane ring were found in the reaction mixture. This observation may indicate a difference in bond strength between the exocyclic and endocyclic P–N bonds. The lower thermodynamic stability of the exocyclic aziridinyl P–N bond, as compared with the endocyclic P–N bond, reflects the sp^3 hybridization of the aziridinyl nitrogen as compared with the nearly planar and highly sp^2 hybridized endocyclic nitrogen and its bond to phosphorus.

The stereoselectivity of fluoride ion toward **1**, as compared to that of chloride and bromide ions, which react with **1** leading exclusively to aziridinyl ring opening and formation of (β-haloethyl)amido derivatives may be rationalized in terms of the known high phosphophilicity of fluoride ion.[12]

Experimental Section

All melting points are uncorrected. Solvents and commercial reagents were distilled and dried by conventional methods before use. $^{31}P[^1H]$ NMR spectra were recorded at 24.3 MHz with a spectrometer equipped with a heterospin decoupler. Positive chemical shift values (ppm) are reported for compounds absorbing at lower fields than 85% H_3PO_4. Mass spectra were obtained at 70 eV ionizing energy (direct inlet). Optical activity measurements were made with a photopolarimeter. Product purities were determined from integrated ^{31}P NMR spectra and TLC (silica gel 60, F_{254}, E. Merck). Silica gel for column chromatography was 100–200 mesh. Solvent systems: A, $CHCl_3$–EtOH (18:1); B, $CHCl_3$–acetone (18:1); C, *n*-hexane–$CHCl_3$–acetone (5:1:2).

2(*S*)-(Ethyleneimino)-2-oxo-3-[(*S*)-α-methylbenzyl]-1,3,2-oxazaphosphorinane (1a) was was obtained according to the published procedure:[1] $^{31}P\delta$ 17.2 (THF); $[\alpha]^{20}_D$ 29.8° (*c* 5, MeOH); mp 121–122 °C (from benzene–*n*-hexane (3:1)); EI MS, *m/z* 266 (M^+, 21), 251 (100), 224 (20), 105 (62); R_f(A) 0.48. **1b** was obtained as the predominant component of an oily mixture **1a,b** containing 69% of **1b** ($^{31}P\delta$ 16.5; R_f(A) 0.48) and 31% of **1a**.

2(*S*)-Fluoro-2-oxo-3-[(*S*)-α-methylbenzyl]-1,3,2-oxazaphosphorinane (4a). *The reaction was performed in a dry box under strictly anhydrous conditions*! Into the solution of **1a** (2.66 g, 10 mmol) in THF (60 mL) was added dropwise, with vigorous stirring at 5 °C poly(hydrogen fluoride–pyridine) [3, 3 mL, Aldrich, HF–C_5H_5N ~20:80 (w/w)]. After 30 min of stirring at 5 °C, the reaction mixture was concentrated under reduced pressure and the oily residue was dissolved in $CHCl_3$ (100 mL). This solution was washed with 10% aqueous $KHCO_3$ (2 × 50 mL), dried over anhydrous $MgSO_4$, and concentrated, and the residue was then introduced on a silica gel column (60 g). The product was eluted with B and fractions containing **4a** (TLC, R_f(B) 0.55) were pooled. Evaporation of solvents gave the crystalline material, which was recrystallized from benzene–*n*-hexane (1:3, 80 mL): yield 50%; mp 113–114 °C; $[\alpha]^{20}_D$ −23.9° (*c*8, C_6H_6); EI MS, *m/z* 243 (M^+, 40), 228 (100), 202 (32), 166 (12). Elemental anal. for $C_{11}H_{15}FNO_2P$. Calcd: C, 54.32; H, 6.22; N, 5.76; P, 12.73. Found: C, 54.08; H, 6.51; N, 6.11; P, 12.69. $^{31}P\delta$−3.2, $^1J_{PF}$ = 966 Hz (C_6H_6).

2(*R*)-Fluoro-2-oxo-3-[(*S*)-α-methylbenzyl]-1,3,2-oxazaphosphorinane (4b). The mixture of **1a** (67%) and **1b** (33%) (1.33 g, 5 mmol, ratio of diastereomers assigned from integrated ^{31}P NMR spectrum) was treated analogously to **1a** (vide supra). The crude material (before chromatographic separation) contained 67% of **4a** and 33% of **4b**: yield 0.8 g (66%). Column chromatography (silica gel, 30 g, eluent C) led to separation of **1a** (R_f(C) 0.40) and **1b** (R_f(C) 0.45). **4b** was crystallized from benzene–*n*-hexane (1:5, 18 mL): yield 0.5 g; mp 91–92 °C; $[\alpha]^{20}_D$ −75.4° (*c*8, C_6H_6); EI MS, *m/z* 243 (M^+, 30), 228 (100), 202 (19), 166 (14). Elemental anal. for $C_{11}H_{15}FNO_2P$. Calcd: C, 54.32; H, 6.22; P, 12.73. Found: C, 54.25; H, 6.33; P, 12.59. $^{31}P\delta$−2.0, $^1J_{PF}$ = 1001 Hz (C_6H_6). The analogous reaction of **1** (**1a** 79%, **1b** 21%) with **3** led to the mixture **4a–4b** (79:21, ^{31}P NMR assay).

Crystal Data for 4a. Crystals are orthorhombic prismatic needles elongated in the *a* direction. The molecular weight is 229.21 daltons and the cell dimensions are a = 6.5238 (6) Å, b = 11.4938 (7) Å, and c = 15.8751 (14) Å (assumed wavelength for CuKα 1.5418 Å). The space group is $P2_12_12_1$ and the calculated density for 4 molecules in the unit cell is 1.279 g cm^{-1}. The larger crystals all proved to have inclusions of solvent, but it was possible to find an apparently perfect needle with dimensions 0.230 × 0.113 × 0.088 mm which was used to collect X-ray intensity data. There were no indications of significant radiation damage and, with a maximum counting time of 60 s, 1420 independent reflection intensities were measured, 334 with $I < \sigma(I)$. The maximum value of $\sin\theta/\lambda$ was 0.6232 Å^{-1}.

Structure Solution and Refinement. The phase problem was solved by means of the programs of MULTAN78[13] which produced an *E* map showing all heavy atoms but for three atoms of the phenyl ring. The missing atoms were found in a weighted Fourier map. The identities of the exocyclic substituents of the P atom could not be deduced at this point and initially both were assigned as oxygen. Refinement, using the programs of XRAY72[14] and anisotropic thermal parameters, reduced the *R* factor to 0.071. At this point separate refinements were made with both F,O assignments. One model gave an *R* factor of 0.069 and a weighted *R* factor of 0.083 and the other produced values of 0.073 and 0.093, respectively. The ratio of the weighted *R* factors is 1.1205 and, with 1086 observations and 145 parameters, the value of χ^2 (0.00001) is 1.1153 thus indicating the model of lower *R* factor. The thermal parameters of the exocyclic F and O atoms were fairly similar in the accepted model whereas, in the other model, one atom had thermal parameters approximately twice as large as the other. All H atoms were found in a weighted difference map. The two possible enantiomers were refined separately with anomalous dispersion coefficients for C, N, O, F, and P and isotropic thermal parameters for the H atoms. The original model refined to an *R* factor of 0.051 and a weighted *R* factor of 0.048 and the enantiomeric model to values of 0.045 and 0.041, respectively. The ratio of weighted *R* factors (1.1572) is sufficiently large to allow acceptance of the model with the lower *R* factor. χ^2 (0.00005) is 1.1546 for 1086 observations and 205 parameters and all discussion corresponds to the indicated enantiomer. It might be noted that the correct enantiomer had lower positional estimated standard deviations for all atoms and positions for H atoms which were more chemically reasonable than those for the other model. Full refinement parameters are available (see paragraph at end of paper concerning supplemental material). The structure factors can be obtained from JVS on request.

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Acknowledgment. This project was in part financially assisted by the Polish National Cancer Program, PR-6, Grant No. 2204.

Registry No. 1a, 72578-60-0; 1b, 72578-64-4; 4a, 95999-19-2; 4b, 95999-20-5.

Supplementary Material Available: Full X-ray refinement parameters (2 pages). Ordering information is given on any current masthead page.

A New Synthetic Route to Tropane Alkaloids Based on [4 + 2] Nitroso Cycloaddition to 1,3-Cycloheptadienes[1]

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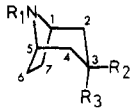
A facile synthesis of tropane, pseudotropine, and tropacocaine is described in which a key step is the Diels–Alder reaction of 1,3-cycloheptadienes with *C*-nitroso compounds to give the 8-oxa-9-azabicyclo[3.2.2]non-6-enes. Reductive treatment involving N–O bond fission of these materials followed by treatment with thionyl chloride gives the trans chlorides or dehydration products which are converted to the tropane alkaloids through intramolecular cyclization induced by a base or mercuric salt, respectively.

The tropane alkaloids occur as esters of relatively simple organic carboxylic acids with amino alcohols (alkamines) which are all hydroxylated derivatives of tropane (**1**), i.e.,

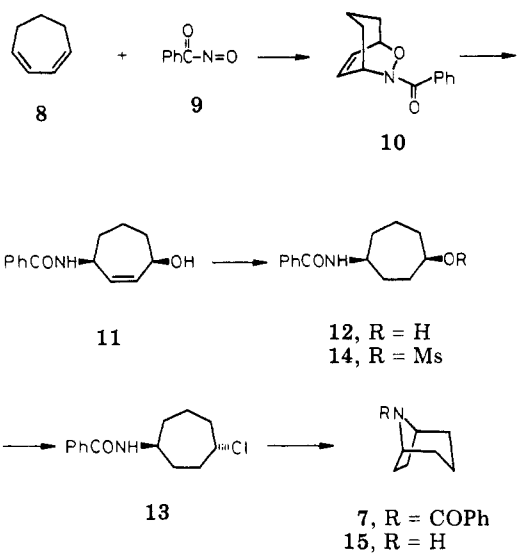


1, $R_1 = CH_3$; $R_2 = R_3 = H$
2, $R_1 = CH_3$; $R_2 = H$; $R_3 = OH$
3, $R_1 = CH_3$; $R_2 = OH$; $R_3 = H$
4, $R_1 = R_2 = H$; $R_3 = OH$
5, $R_1 = CH_3$; R_2, $R_3 = O$
6, $R_1 = CH_3$; $R_2 = OCOPh$; $R_3 = H$
7, $R_1 = COPh$; $R_2 = R_3 = H$

tropine (**2**), pseudotropine (**3**), and nortropine (**4**) as monohydroxylated alkamines. Because of their pharmaceutical significance and the presence of an unusual ring system, this class of alkaloids have been the subject of intensive stereochemical, biogenetical, and synthetic activities.[2] In particular, a great deal of synthetic work on natural and nonnatural tropane bases has been carried out with the aim of investigating their pharmacological activity. The earliest synthetic approach to a tropane base was described by Willstätter.[2a] This approach to tropinone (**5**) in a multistage synthesis was followed by a more lucid and practical Robinson synthesis.[3] Since these classical syntheses of tropinone (**5**), a number of general synthetic methods for the preparation of some tropanes have been reported. However, except for two instances of new approach to tropane alkaloids via [3 + 2] nitrone cycloaddition[4] and [3 + 4] cyclocoupling,[5] efficient methods for the preparation of natural products are limited.

In this paper we describe a facile new route for the elaboration of the tropane ring system by utilizing a

Scheme I



Diels–Alder cycloaddition of nitroso compounds[6] with 1,3-cycloheptadienes and its application to the synthesis of the naturally occurring tropane alkaloids pseudotropine (**3**) and tropacocaine (**6**).

Results and Discussion

Synthesis of *N*-Benzoylnortropane. As our first model we chose *N*-benzoylnortropane (**7**) to investigate construction of the tropane ring system based on [4 + 2] nitroso cycloaddition. A search of the literature indicated that only one example of a Diels–Alder cycloaddition of a nitroso compounds with a seven-membered ring diene has been reported.[7] In view of this, the present study of tropane synthesis was initiated by the examination of the nitroso Diels–Alder reaction of 1,3-cycloheptadiene (**8**) (Scheme I). Thus reaction of **8** with the acylnitroso compound **9** generated in situ from benzohydroxamic acid

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