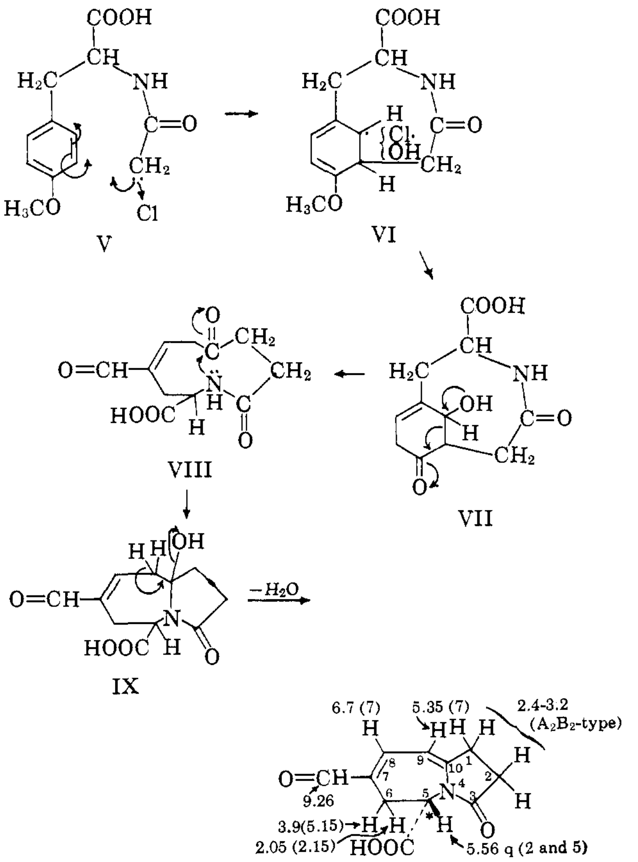
Chart I[a]



IV, R = CH_3
X, R = H
(L or *S* configuration)

[a] Values in parentheses are coupling constants, measured in cycles per second.

hydroxyl (IX) would then yield L-5-carboxy-7-formyl-1,2,5,6-tetrahydro-3H-pyrrolo[1,2-*a*]azepin-3-one (X).

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The Unstable Arsinoboron Heterocycle $[(CF_3)_2AsBH_2]_3$[1]

Sir:

The chemical bonding principle first illustrated by the very stable trimer $[(CH_3)_2PBH_2]_3$[2] was extended beyond all expectations by the discovery of $[(CF_3)_2PBH_2]_3$ (stable to 200°),[3] for the existence of which the ring P→B dative bonding alone would not seem to offer an adequate explanation. We now report the discovery of an even less expected analog: the arsenic–boron ring compound $[(CF_3)_2AsBH_2]_3$.

Synthesis. This new trimer was made by mild heating of $(CF_3)_2AsH$[4] with B_2H_6 (stabilized by 1 atm pressure of H_2) in a sealed bulb. Most simply, one heats the bottom of the bulb to 40–45° while the top remains at 25° or lower. Within 3–4 days, a trace of a white sublimate will indicate undesirable effects, and the process is stopped. The components are separated completely by high-vacuum fractional condensation, with the desired trimer trapping out at −10° in yields as high as 70% of the consumed reactants. A better way is to heat one side of the bulb to 50–60° by an electric blade, while keeping the bottom at 0°. Convection moves the forming trimer to the 0° region, where it condenses and is stable. One such run (8.5 days) went as follows (millimole stoichiometry).

Table I. Volatility of Liquid $[(CF_3)_2AsBH_2]_3$
($\log P = 11.0454 + 1.75 \log T - 0.0100T - 3754/T$)
($t_{760} = 178.2°$; Trouton constant = 21.2 eu)

Temp, °C	26.4	28.0	30.0	32.2	34.1	35.9
P_{obsd}, mm	0.69	0.80	0.94	1.11	1.32	1.47
P_{calcd}, mm	0.71	0.83	0.94	1.11	1.28	1.47

$$\begin{array}{cccc} 6(CF_3)_2AsH & + \ 3B_2H_6 & \longrightarrow 6H_2 & + \ 2[(CF_3)_2AsBH_2]_3 \\ 0.9731 & 1.892 & \ldots & 0.243 \\ \underline{-0.1178} & \underline{-1.442} & & (85\% \text{ of As}) \\ 0.8553 & 0.450 & & \end{array}$$

A less volatile crystalline by-product probably was $[(CF_3)_2AsBH_2]_4$, for its infrared spectrum (weak at 2490 and 2415 cm^{-1}; strong at 1178, 1148, and 1108 cm^{-1}; medium at 949 and 738 cm^{-1}) was very like that of the trimer when allowance is made for lower frequencies in a Nujol mull.

Characterization. The short melting range (3.0–3.5°) of the trimer and its consistent vapor tensions (Table I) were indicative of purity.

Thermal decomposition to $(CF_3)_2AsH$, BF_3, and nonvolatile solids made it difficult to work with this trimer above 40°. However, one sample was heated for 1 week at 55–60° with 600 mm pressure of hydrogen, showing only 30% decomposition and apparent inhibition of formation of BF_3. Dry HCl failed to affect it while it decomposed slightly during 70 hr at 25°.

The vapor-phase molecular weight was determined by means of a 630-ml immersible tensimeter, in which a sample large enough for accurate weighing all evaporated to register 2 mm pressure, read to 0.01 mm. The average result of four readings (45–51°) was 682 (mean deviation 4.3); calculated, 677.

Proof of Formula. A weighed 0.0969-mmole sample of the trimer reacted with methanol and HCl (98°, 24 hr), forming 0.280 mmole of $(CF_3)_2AsH$ and 0.546 mmole of H_2, respectively 96 and 94% of the calculated values. The excess methanol formed some CH_3Cl, from which the $(CF_3)_2AsH$ could not be completely isolated; hence this arsine was determined by comparing the intensity of its 2142-cm^{-1} infrared peak with that of a known sample at a similar pressure and path length. The slight deficiency of H_2 and $(CF_3)_2As$ groups correlated with a trace of a brown decomposition product.

For boron and confirmation of hydrogen, a 29.8-mg sample (0.132 mmole) was exposed to pure chlorine in excess. Heating to 70° caused a sudden soot formation; then the tube was heated to 400° to make sure of complete reaction. Mercury removed the excess Cl_2 and the most volatile fraction was isolated by passage through a high-vacuum trap at −140°. No BCl_3 could be found. The product BF_3 was isolated

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[1] It is a pleasure to acknowledge the support of this research by the Office of Naval Research, through Contract No. Nonr-228(13), Task Order NR 052 050. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

[3] A. B. Burg and G. Brendel, *ibid.*, **80**, 3198 (1958).

[4] Made by the two methods described by W. R. Cullen, *Can. J. Chem.*, **39**, 1855 (1961).

Table II. Comparison of Infrared Spectra[a]

Assignment	$(M_2AsBH_2)_3$	$(M_2PBH_2)_3$	$(M_2PBD_2)_3$
B–H stretching	2530 (6.5)	2514 (2)	1889 (1.1)
	2449 (3.9)	2429 (0.6)	1794 (0.9)
C–F stretching	1190 (410)	1206 (170)	1205 (400)
	1154 (160)	1192 (167)	1192 (265)
	1123 (145)	1164 (100)	1164 (160)
BH_2 deformation?	1075 (5.3)	1152 w, sh	952 w
			852 w
BH_2 out-of-plane rock	960 (33)	995 (4)	755 (1.6)
CF_3 sym deformation	742 (20)	764 (0.8)	761 sh (1.2)
BH_2 in-plane rock	636 ? w	715 (17)	566 (9)
CF_3 asym deformation	(Too weak)	538 (3.6)	532 (2.0)
As–CF_3 stretching	332 (17)	. . .	. . .
P–CF_3 stretching	. . .	455 (6)	444 (6)
		436 (7)	431 (5)
		414 (5)	409 (0.7)
Uncertain		659 (10)	662 (12)
		621 (3)	602 (20)
		554 (1.5)	395 (2.2)

[a] M = CF_3; w = weak; sh = shoulder.

through formation of its acetyl chloride complex at −110°, and HCl was similarly removed as the $(CH_3)_2O$ complex, leaving a trace of SiF_4. The result was 2.06 HCl and 1.04 BF_3 (both ±5%) per calculated $(CF_3)_2$-$AsBH_2$ unit. Thus the elementary analysis was complete, fully confirming the formula $[(CF_3)_2AsBH_2]_3$.

Infrared Spectra. The frequencies (cm^{-1}) of the infrared fundamental peaks observed for $[(CF_3)_2AsBH_2]_3$ in the vapor phase at 1.2 mm pressure (33°) are compared with the analogous peaks for $[(CF_3)_2PBH_2]_3$ and $[(CF_3)_2PBD_2]_3$ in Table II. The relative intensity appears in parentheses after each frequency.

Discussion. The 960-cm^{-1} peak for BH_2 out-of-plane rocking fits a previously recognized trend.[5] By comparison with the 812-cm^{-1} peak observed for $[(CH_3)_2PBH_2]_3$ and other pertinent data for such compounds, the 995-cm^{-1} peak suggests that the HBH angle in $[(CF_3)_2PBH_2]_3$ might be as much as 10° wider than the 119.3° reported for $[(CH_3)_2PBH_2]_3$.[6] Also, two different methods estimate the HBH angle as 2.5 to 2.8° narrower in $[(CF_3)_2AsBH_2]_3$ than in $[(CF_3)_2PBH_2]_3$. The latter comparison would agree with the expectation that As_{4d} would be less effective than P_{3d} for interaction with B–H bonding electrons, but in both cases such interactions, involving 12 electrons and 6 highly contracted d orbitals, would have important ring stabilizing effects.

(5) A. B. Burg, *Robert A. Welch Found. Conf.*, **6**, 142 (1962). In that lecture this mode was called "wagging." Also, the BD_2 in-plane rocking is reassigned to 566 cm^{-1} without affecting the argument.

(6) W. C. Hamilton, *Acta Cryst.*, **8**, 199 (1955).

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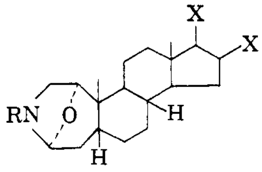
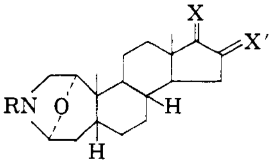
A Total Synthesis of Samandarone

Sir:

Salamander alkaloids were found in the toxic secretion of the alpine salamander by Zalesky in 1866.[1] Samandarine was isolated as a main component of these alkaloids, and its structure has been suggested by Schöpf and his colleagues to be Ia through chemical, optical, and X-ray crystallographic studies.[1-3] The characteristic skeleton of samandarine is common to four other alkaloids, *i.e.*, samandarone (IIa),[2] samandaridine,[4] O-acetylsamandarine,[5] and samandesone,[6] which differ from each other only in the D-ring substituent. We wish to record the total synthesis of samandarone, which will be a general intermediate for the preparation of structurally similar alkaloids.

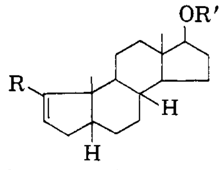


Ia, R = X = H; X′ = OH
b, R = $PhCH_2$; X = OH; X′ = H
c, R = X′ = H; X = OH

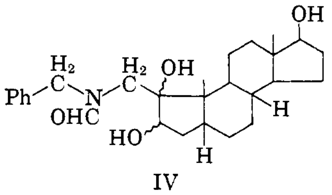


IIa, R = H; X = H_2; X′ = O
b, R = PhCO; X = H_2; X′ = O
c, R = $PhCH_2$; X = O; X′ = H_2
d, R = H; X = O; X′ = H_2
e, R = CHO; X = O; X′ = H_2
f, R = CHO; X = O; X′ = CHOH
g, R = CHO; X = O; X′ = CHO-*i*-Pr
h, R = CHO; X = $<^{H}_{OH}$; X′ = CHO-*i*-Pr
i, R = CHO; X = H_2; X′ = CHOAc

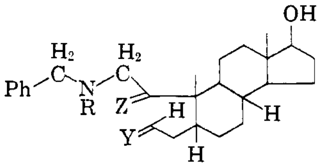
1-Formyl-A-nor-5β-androst-1-en-17β-ol (IIIa) was prepared from testosterone as described in a previous paper.[7] The benzylamino Schiff base of IIIa was reduced with sodium borohydride to give the unsaturated amine IIIb.[8] After protection of the amino group as the formamide IIIc (mp 130–132°),[9] the double bond was oxygenated with osmium tetroxide in diethyl ether–pyridine to afford the *cis*-glycol IV, which formed a crystalline acetonide (mp 248–250°). The glycol IV was cleaved by lead tetraacetate to give the seco-aldehyde Va (δ 9.60 (triplet, C*H*O), 8.33 (singlet, N-C*H*O), 7.30 (5 aromatic *H*), 4.39 and 4.07 (unresolved multiplet N(CH_2)$_2$, respectively), 2.42 (unresolved



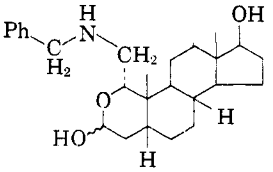
IIIa, R = CHO; R′ = H
b, R = $PhCH_2NHCH_2$; R′ = H
c, R = $PhCH_2N(CHO)CH_2$; R′ = CHO



IV



Va, R = CHO; Y = O; Z = O
b, R = CHO; Y = $<^{O\urcorner}_{O\lrcorner}$; Z = O
c, R = CHO; Y = $<^{O\urcorner}_{O\lrcorner}$; Z = $<^{H}_{OH}$
d, R = H; Y = $<^{O\urcorner}_{O\lrcorner}$: Z = $<^{H}_{OH}$



VI

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(1) The review of these alkaloids is in C. Schöpf, *Experientia*, **17**, 285 (1961), and G. Habermehl, *Naturwissenschaften*, **53**, 123 (1966).

(2) E. Wölfel, C. Schöpf, G. Weitz, and G. Habermehl, *Chem. Ber.*, **94**, 2361 (1961).

(3) G. Habermehl, *ibid.*, **96**, 143 (1963).

(4) G. Habermehl, *ibid.*, **96**, 840 (1963).

(5) G. Habermehl, *Ann.*, **679**, 164 (1964).

(6) G. Habermehl, *Chem. Ber.*, **99**, 1439 (1966).

(7) S. Hara and K. Oka, *Tetrahedron Letters*, 1057 (1966).

(8) Infrared spectra for all reported compounds were taken with KBr tablets and are consistent with assigned structures.

(9) Satisfactory analytical data were obtained for crystalline compounds.