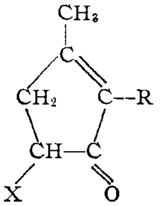
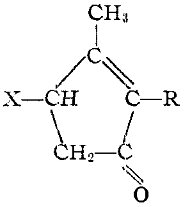
Bromosuccinimide also substitutes bromine on methylene groups *alpha* to carbonyls of saturated cyclic and acyclic ketones[3] and of α,β-unsaturated ketones of the mesityl oxide type[4] but substitutes on the allylic methylene of Δ^4-3-ketosteroids.[5]


Ia, R = *n*-Bu, X = OH
Ib, R = *n*-Am, X = OH


IIa, R = *n*-Bu, X = OH
IIb, R = *n*-Am, X = OH
IIc, R = *n*-Am, X = Br

Prior to publication of the dihydrocinerolone synthesis,[1] we had employed the N-bromosuccinimide reaction for the synthesis of the homologous *dl*-tetrahydropyrethrolone. Its identity with the natural product has now been established and additional evidence obtained to support the contention of allylic bromination and β-ketol structure. The slow reaction of tetrahydropyrethrolone with periodic acid (2.8–3.2% equivalent in forty-eight hours) indicates the absence of an α-ketol structure (Ib),[6] and as a consequence the β-ketol structure (IIb), proposed by LaForge and Soloway,[1] becomes the most likely structure for tetrahydropyrethrolone.

Reaction between equimolar quantities of tetrahydropyrethrone and N-bromosuccinimide in carbon tetrachloride was complete after thirty minutes of heating under reflux. Distillation of the filtered solution gave 67% yield of bromoketone (IIc), b. p. 115–122° (2.2–2.3 mm.), $n^{25}\mathrm{D}$ 1.5100, which, on refluxing for four hours with silver acetate in glacial acetic acid, gave *dl*-tetrahydropyrethrolone acetate in 70% yield, b. p. 120–123° (1.0–1.4 mm.), $n^{26}\mathrm{D}$ 1.4755 (calcd. for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.7; H, 9.24); semicarbazone, m. p. 85–86°; *p*-nitrophenylhydrazone, m. p. 146°. The only constants reported are for the *d*-enantiomorph, b. p. 117° (1.3 mm.), $n^{20}\mathrm{D}$ 1.4761.[7] Deacetylation by heating overnight with an aqueous barium carbonate suspension gave slightly impure *dl*-tetrahydropyrethrolone in 54% yield, b. p. 110–112° (0.3 mm.), $n^{28}\mathrm{D}$ 1.4990; but similar hydrolysis of undistilled bromotetrahydropyrethrone gave purer *dl*-tetrahydropyrethrolone in 35% yield, b. p. 118–120° (0.3 mm.), $n^{25}\mathrm{D}$ 1.4921, Fehling test on warming, no solid osazone (calcd. for $C_{11}H_{18}O_2$: C, 72.53; H, 9.98. Found: C, 71.1; H, 9.74, average of three analyses); 3,5-dinitrobenzoate, m. p. 105–105.5° (calcd. for $C_{18}H_{20}O_7N_2$: C, 57.44; H, 5.36. Found: C, 57.3; H, 5.05); semicarbazone, m. p. 170.2–170.6° (calcd. for $C_{12}H_{21}O_7N_2$: C, 60.22; H, 8.85. Found: C, 60.4; H, 8.60), absorption maximum at 2635 Å., ε = 23,200 in ethanol; methyl ether semicarbazone, m. p. 122.5–123°. The best constants reported are: tetrahydropyrethrolone, b. p. 135–136° (1 mm.),[8] $n^{20}\mathrm{D}$ 1.4900–1.4907[8]; *dl*-semicarbazone, m. p. 172–173°,[8] 171–173°,[9] absorption maximum at 2650 Å., ε = 22,700[9]; *dl*-methyl ether semicarbazone, m. p. 122–123°.[7]

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(3) Schmid and Karrer, *Helv. Chim. Acta*, **29**, 573 (1946); Djerassi and Scholz, *Experientia*, **3**, 107 (1947).

(4) Buu-Hoï, *ibid.*, **2**, 310 (1946).

(5) Meystre and Wettstein, *ibid.*, **2**, 408 (1946).

(6) Clutterbuck and Reuter, *J. Chem. Soc.*, 1467 (1935).

(7) Gillam and West, *ibid.*, 645 (1944).

(8) LaForge and Barthel, *J. Org. Chem.*, **10**, 117 (1945).

(9) West, *J. Chem. Soc.*, 463 (1946).

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RECEIVED MAY 31, 1947

ELECTRON DEFICIENT COMPOUNDS. III. THE BRIDGE STRUCTURE FOR B_2H_6

Sir:

Recently Burg has shown that there are no acidic hydrogens in B_2H_6,[1] and suggests that adoption of the "protonated double bond"[2] structure is inadvisable. Though they make the term "protonated" inappropriate, Burg's experiments do not invalidate the bridge structure. They do help settle the type of bonding in the bridge, if the bridge model is accepted.

It can be shown[3] that a hydrogen atom can be more strongly bound by one electron pair through two boron orbitals than one. The bond energy of a B–H–B bridge may well be of the order of 30% greater than a B–H bond.[3] Hence, the bridge hydrogens should not be acidic.

Pitzer[2] did not state what a "protonated double bond" meant in terms of bond orbitals. One interpretation is that sp^2 orbitals of each boron are used to form two B–H bonds and one B–B bond. The p-orbitals from each boron might then overlap with the s-orbital of hydrogens above and below the plane of the molecule. Then one electron pair would bind two hydrogens, which would carry formal charges $(+{}^1/_2)$, would be weakly bound and acidic.

In another interpretation tetrahedral orbitals of boron are used, with each bridge hydrogen at the intersection of orbitals from each boron, and no boron–boron bond.[3] Since the B–H bond energy is greater than the B–B, and since no formal charges are introduced, this structure must

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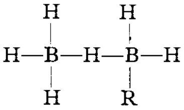
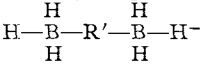
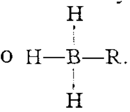
(1) A. Burg, THIS JOURNAL, **69**, 747 (1947).

(2) K. S. Pitzer, *ibid.*, **67**, 1126 (1945).

(3) R. Rundle, "Electron Deficient Compounds I and II," submitted for publication in THIS JOURNAL. This concept was presented before the Division of Physical and Inorganic Chemistry, The American Chemical Society Convention, April, 1947.

be stable with respect to the first. Since the molecular geometry is similar, both electronic structures may contribute, with the second predominating. Burg's results support a high predominance of the second structure.

Furthermore, the bridge model is capable of including the borine-complex theory of the base reactions of B_2H_6. A molecule with unshared pair, :R, (:NH_3, :$N(CH_3)_3$ ethers, etc.) may attack B_2H_6 from the back side of one of the bridge bonds, leading to  $\mathrm{H{-}\overset{H}{\underset{H}{B}}{-}H{-}\overset{H}{\underset{R}{B}}{-}H}$ (I). If :R contains an acidic hydrogen, (I) may be quickly converted to  $\mathrm{H{-}\overset{H}{\underset{H}{B}}{-}R'{-}\overset{H}{\underset{H}{B}}{-}H^-}$ ($R' + H^+ =$:R) plus (H:R)$^+$. (This appears to happen with NH_3 but not with $N(CH_3)_3$.) If R does not lose a proton readily, then I may be attacked by another :R, leading to  $\mathrm{H{-}\overset{H}{\underset{H}{B}}{-}R}$.

The proposed attack of B_2H_6 by :R resembles the attack in a Walden inversion, but activation energies should be much lower, rates much higher, since the serious repulsive terms in Walden inversion arise from completed electron shells. A tetrahedral configuration about boron is not objectionable in the above process. It would appear that the bridge model is as satisfactory as any proposed for the interpretation of the reactions B_2H_6 with ammonia and amines.

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RECEIVED MAY 9, 1947

ENRICHMENT OF C^{13} AND O^{18} BY A COUNTERCURRENT GASEOUS EXCHANGE PROCESS USING THERMAL DIFFUSION

Sir:

Using the exchange reaction[1] $C^{13}O + C^{12}O_2 = C^{12}O + C^{13}O_2$ in conjunction with a thermal diffusion column, an enrichment of both C^{13} and O^{18} has been effected. This system is unique in that the thermal diffusion column establishes a countercurrent flow of the two gases between which the exchange takes place. The hot element produces the thermal diffusion and also serves as a catalytic surface for the exchange.[2]

The column consisted of a 1.0-cm. diameter water-jacketed tube 110 cm. long, at the top of which was connected a 20-liter reservoir of carbon dioxide at atmospheric pressure. Platinum filaments were found more satisfactory than either nichrome or tungsten. A hot zinc converter and a thermal conductivity cell at the bottom of the column had a total volume of about 200 cc. Total reflux was obtained by recirculating the carbon dioxide through the converter. The thermal conductivity cell indicated that practically complete conversion to carbon monoxide took place, thus establishing the condition of total reflux. By measuring the buildup rate of carbon monoxide in the reservoir, its transport up the column was found to be approximately 1.0 cc./minute. The carbon monoxide rising up the column undergoes isotopic exchange with descending carbon dioxide. Since the exchange reaction favors the transfer of C^{13} and O^{18} to carbon dioxide, the heavy carbon and oxygen concentrate at the bottom of the column.

The data for three of the experiments are summarized in Table I. The enrichments were measured with a Nier type mass spectrometer to ±1.0 in the percentage enrichment.

TABLE I

Expt.	Filament	Current, amps.	*T*, °C. (approx.)	Time, days	% Enrich. C^{13}	% Enrich. O^{18}
1	Nichrome	2.75	700	2.0	4.0	..
				3.0	6.5	..
				4.0	9.5	..
				5.0	10.5	..
				7.0	14.0	..
2	Platinum	3.2	800	1.0	9.0	9.0
				2.0	9.0	..
3	Pt + H_2O	3.2	800	1.2	14.0	..
				2.2	23.5	18.0

Since water and hydrogen have been shown[1] to be effective catalysts for the exchange, a small supply of water was introduced at the bottom of the column in experiment 3. The results show a higher isotope enrichment.

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[1] See Urey and Greiff, THIS JOURNAL, **57**, 321 (1935), and Braudner and Urey, *J. Chem. Phys.*, **13**, 351 (1945).

[2] Clusius and Dickel, *Z. physik. Chem.*, **B44**, 397 (1939).

SPECTROPHOTOMETRIC INVESTIGATION OF THE INTERACTION BETWEEN IONS OF DIFFERENT OXIDATION STATES OF AN ELEMENT

Sir:

It has often been remarked that systems containing an element in two different oxidation states or in a "mixed" oxidation state sometimes manifest abnormally deep and intense coloration.[1]

The concentration dependence of this phenomenon has been investigated with a Beckmann spectrophotometer for mixed solutions of tri- and pentavalent antimony in concentrated hydrochloric acid; in addition, the hitherto unreported occurrence of such an "interaction absorption" for mixed stannous-stannic solutions in concentrated hydrochloric acid has been observed.

The figure illustrates the absorption spectra of such mixed solutions and of the components. The optical density of interaction color in the antimony solutions is proportional to the product

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[1] *E. g.*, Biltz, *Z. anorg. allgem. Chem.*, **127**, 169 (1923).