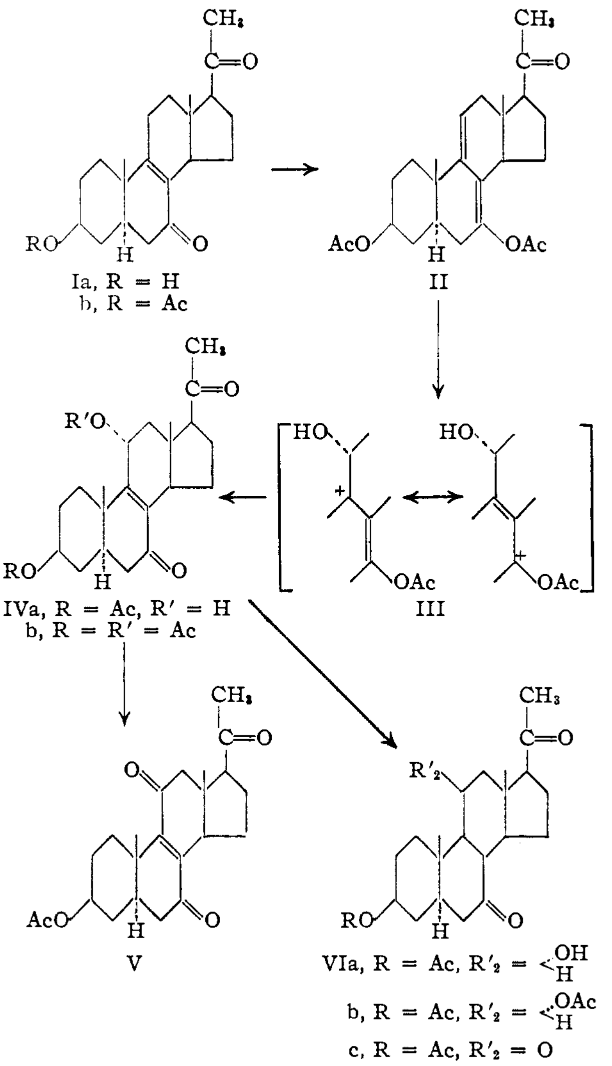

allopregnene-7,20-dione-3β,11α-diol diacetate (IVb) (m.p. 216–218°, $[\alpha]\mathrm{D}^{20}$ +55°, $\lambda_{\max.}^{\mathrm{EtOH}}$ 252 mμ, log ε 4.07, $\lambda_{\mathrm{CHCl}_3}$ 1728 (acetate), 1700 (20-ketone) and 1670 cm.$^{-1}$ (Δ^8-7-ketone), found: C, 69.65; H, 7,98) and then hydrogenated to allopregnane-7,20-dione-3β,11α-diol diacetate (VIb) (m.p. 156–157°, $[\alpha]^{20}\mathrm{D}$ ± 0°, $\lambda_{\max.}^{\mathrm{CS}_2}$ 1736 (acetate), 1718 (7-ketone) and 1710 cm.$^{-1}$ (20-ketone), found: C, 69.37; H, 8.52).

Saponification of the performic acid oxidation mother liquors yielded $\Delta^{8(9)}$-allopregnene-7,20-dione-3β-ol (Ia) (m.p. 191–193°, $[\alpha]^{20}\mathrm{D}$ −8°, $\lambda_{\max.}^{\mathrm{EtOH}}$ 252 mμ, log ε 4.10, $\lambda_{\max.}^{\mathrm{nujol}}$ 1700 and 1656 cm.$^{-1}$ and free hydroxyl band, found: C, 76.50; H, 9.28); acetate (Ib), (m.p. 159–161°, $[\alpha]^{20}\mathrm{D}$ −12°, found: C, 74.13; H, 8.91), which presumably arose from a mixture of $\Delta^{9(11)}$-7,8-oxides and/or $\Delta^{9(11)}$-7-one, since chromatography of the mother liquors produced in a fair state of purity two isomers ($C_{23}H_{32}O_4$) giving a yellow color with tetranitromethane (*A*: m.p. 139–142°, $[\alpha]^{20}\mathrm{D}$ +33°, found: C, 74.49; H, 9.03; *B*: 213–215°, $[\alpha]^{20}\mathrm{D}$ −35°, found: C, 73.43; H, 8.79), which were rearranged by alkali in high yield to the identical unsaturated ketone Ia. *Taking advantage of the fact that isopropenyl acetate*[4a] *reacts readily with α,β-unsaturated ketones but not at all with saturated 20-ketosteroids*, the acetate Ib was converted to the oily enol acetate II, which without isolation was treated with 1.1 moles of monoperphthalic acid in ether solution at room temperature. After 40 hours, there *crystallized directly*[5] from the ether solution in over 70% over-all yield (based on Ib) $\Delta^{8(9)}$-allopregnene-7,20-dione-3β,11α-diol 3-monoacetate (IVa) (m.p. 192–194°, $[\alpha]^{20}\mathrm{D}$ +14°, $\lambda_{\max.}^{\mathrm{EtOH}}$ 252 mμ, log ε 4.12, $\lambda_{\max.}^{\mathrm{CHCl}_3}$ 1728, 1700 and 1670 cm.$^{-1}$ and free hydroxyl band, found: C, 71.29; H, 8.39), which upon acetylation gave the identical diacetate IVb described above. Hydrogenation of IVa with palladized charcoal afforded 81% of allopregnane-7,20-dione-3β,11α-diol 3-acetate (VIa) (m.p. 184–186°), $[\alpha]^{20}\mathrm{D}$ −10°, $\lambda_{\max.}^{\mathrm{nujol}}$ 1736, 1718 and 1700 cm.$^{-1}$ and free hydroxyl band, found: C, 70.96; H, 8.85), identified further by conversion to the known (*vide supra*) 3,11-diacetate VIb.

A particularly attractive feature of the present process is the facile preparation of 3-acylated-11α-ols (*e.g.*, IVa, VIa), which allows interconversion with intermediates employed by other workers[3,6] for the introduction of an 11-keto group. As an illustration, chromium trioxide oxidation of the monoacetate IVa smoothly yielded $\Delta^{8(9)}$-allopregnene-7,11,20-trione-3β-ol acetate (V) (m.p. 171–173°, $[\alpha]^{20}\mathrm{D}$ +50°, $\lambda_{\max.}^{\mathrm{EtOH}}$ 268 mμ, log ε 3.82, found: C, 71.63; H, 8.06), while similar treatment of VIa afforded allopregnane-7,11,20-trione-3β-ol acetate (VIc) (m.p. 209–211°, $[\alpha]^{20}\mathrm{D}$ +20°, found: C, 71.25; H, 8.40).

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RECEIVED AUGUST 6, 1951

[4a] In benzene solution, using *p*-toluenesulfonic acid as catalyst.

[5] The reaction presumably involves attack of the unhindered 11α-position by positively charged hydroxyl ion (*cf.* D. Swern, *Chem. Revs.*, **45**, 48 (1949)) through species such as III to yield ultimately IVa and possibly the mixed anhydride of phthalic and acetic acids. An analogous change is involved in the conversion of thebaine to 14-hydroxycodeinone (M. Freund and E. Speyer, *J. prakt. Chem.*, **94**, 135 (1916)) by peracetic acid.

[6] E. M. Chamberlin, W. V. Ruyle, A. E. Erickson, J. M. Chemerda, L. M. Aliminosa, R. L. Erickson, G. E. Sita and M. Tishler, THIS JOURNAL, **73**, 2396 (1951).

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THERMAL DECOMPOSITION OF CYCLOBUTANE

Sir:

Cyclobutane has been found to undergo a homogeneous, first order decomposition in the temperature range 430–480°. The cyclobutane which was prepared by the photolysis of cyclopentanone[1,2] was purified by fractionation in a Podbielniak column. Samples obtained by fractionation and subjected to different purification treatments have given similar results. Infrared absorption curves[3] and vapor pressure measurements have been used to confirm the identity and purity of the cyclobu-

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[1] S. Benson and G. Kistiakowsky, THIS JOURNAL, **64**, 80 (1942).

[2] This preparation was undertaken jointly with Drs. L. H. Jones and A. B. F. Duncan.

[3] The infrared absorption measurements have been made by Mr. Carl Whiteman.

tane.[4] Ethylene, which was observed to be an impurity before fractionation, could not have been present in more than a very small percentage after fractionation. Moreover, the rate was not altered appreciably by the addition of ethylene (Table I).

TABLE I

Sample I, vap. press. at 0° = 467 mm. compared with 466.5 mm. calculated by Heisig's equation; Ia, refluxed with freshly distilled sodium; Ib, refluxed over silver oxide; IIa, passed over concd. sulfuric acid, vap. press. at −7.7° = 338.5 mm. compared with 337 mm. calculated by Heisig's equation. $t_{1/4}$ = time for the pressure increase to reach 25% of the maximum pressure increase. C_3H_6 = propylene.

Temp., °C.	$P^0_{C_4H_8}$, mm.	Sample	Added subst.	$P_{A.S.}$ mm.	$t_{1/4}$, min.
438	125	I	...	0	18.9
438	124	Ib	...	0	18.8
438	106	I	C_2H_4	23	19.3
438	112	IIa	...	0	18.6
449	33	I	...	0	10.6[a]
449	106	Ia	...	0	9.7
449	129	I	...	0	9.8
449	406	I	...	0	9.8
459	68	I	C_3H_6	43	5.4
459	88	I	...	0	5.3
459	110	I	NO	3.3	5.2

[a] Average of three runs; for all runs at 449° the time for 24.4% pressure increase (cor. for dead space) has been taken as $t_{1/4}$.

The fact that the ratios of the maximum final pressure to the initial pressure are 2.00, 1.98 and 1.97 (corrected for dead space) at 482, 459 and 438°, respectively, indicates that two molecules are formed from each cyclobutane molecule. There are indications that a subsequent reaction of the products which produces a very slow pressure decrease may be at least partly responsible for the difference in P_f/P_0 at the lower temperatures where the attainment of the final pressure is slow. The infrared absorption curve for the products at complete decomposition indicates that ethylene is practically the sole product. This finding is in agreement with the observations that 99% of the mixture in the reaction zone at maximum pressure increase is condensable at −196°, not more than 3% is condensable at −78°, and about 95% is absorbable in activated sulfuric acid.[5] The over-all reaction appears to be $C_4H_8 = 2\ C_2H_4$.

During the decomposition the pressure increases in the manner expected for a first order reaction (with no induction period). By calculation of the amount of reaction from the pressure measurements and the observed over-all pressure increase, the ratio of $t_{1/2}/t_{1/4}$ averaged 2.39 in comparison with 2.41 for a first order reaction and a linear plot of log $P_{C_4H_8}$ *vs.* time was obtained over essentially the entire reaction. For the experiments at 449° shown in Table I the fractional times appear to be approximately the same for the range 100–400 mm. The reaction has been carried out in an unpacked Pyrex vessel with and without potassium chloride coating, in a packed Pyrex vessel, and in a silica vessel.[6] The results have shown that the decomposition does not depend to a significant extent upon the nature or the amount of the surface. No evidence for a chain reaction has been obtained yet, but this matter will be investigated. Preliminary data indicate the activation energy is about 61 kcal./mole.

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RECEIVED JULY 31, 1951

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[4] T. P. Wilson, *J. Chem. Phys.*, **11**, 369 (1943); J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949); G. B. Heisig, *ibid.*, **63**, 1698 (1941).

[5] W. J. Gooderham, *J. Soc. Chem. Ind. (London)*, **57**, 388T (1938).

[6] D. A. Bittker and H. D. Batha have assisted in these studies.

THE USE OF SODIUM CYANIDE WITH L-ARABINOSE IN THE KILIANI SYNTHESIS

Sir:

When hexonic acids are synthesized from L-arabinose by the Kiliani method, using aqueous hydrocyanic acid, L-mannonic acid is the principal product with only a minor amount of L-gluconic acid.[1] We have observed that if the cyanide addition is carried out in a cold aqueous solution of sodium cyanide L-gluconic acid is the principal product with only a minor amount of L-mannonic acid. This reversal of proportions of diastereoisomers does not occur, however, with all reducing sugars; thus D-glucose yields about the same ratio of D-gluco-D-*gulo*-heptonic acid to D-gluco-D-*ido*-heptonic acid with either hydrocyanic acid or sodium cyanide. Since it thus becomes evident that any generalization relating the configuration of an aldose with that of the next higher aldonic acid diastereoisomer that is favored in the cyanide synthesis must specify the method of addition, it is emphasized that the Maltby rule which I have discussed[2] is to be understood as applying to syntheses in which aqueous hydrocyanic acid reacts with aldoses.

The experimental procedure for preparing L-gluconic acid (as its barium salt) from L-arabinose and sodium cyanide involves only one major change from the directions of E. Fischer for L-arabinose and hydrogen cyanide; this consists in the removal of sodium ions at the proper stage by an ion-exchange column. An ice-cold solution containing 30 g. of pure L-arabinose and 13 g. of sodium cyanide in 300 ml. of water was kept near +5° in a refrigerator until the Fehling test became faint (4 days). Barium hydroxide (10 g. of octahydrate) was added and the solution was boiled with renewal of water to expel all ammonia (3 to 4 hours). The barium was then removed as carbonate after addition of activated carbon and the sodium ions were adsorbed by passing the solution through an ion-exchange column. Concentration to a sirup, lactonization and solution of the residue in methyl cellosolve led to only 2.5 g. of crystalline L-mannonic γ-lactone. Removal of solvent from the mother liquor, conversion of the acidic residue to its neutral barium salt and crystallization from aqueous ethanol[3] produced 26.1 g. of barium L-gluconate (anhydrous basis). Its $[\alpha]^{20}D$ was −6.4° (*c* 8.7 g./100 ml. aqueous soln.) in agreement with the value for barium D-gluconate (+6.1). (Kiliani found that even pure barium L-mannonate would not crystallize and our experience confirms this observation.) Removal of barium ions from the mother

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[1] E. Fischer, *Ber.*, **23**, 2611 (1890).

[2] C. S. Hudson, *Advances in Carbohydrate Chem.*, **1**, 26 (1945).

[3] H. Kiliani, *Ber.*, **58**, 2350 (1925); **59**, 1470 (1926).