(*Anal.* Calcd. for $C_6H_{15}O_3N_5Cl_2$: N, 25.37; Cl, 25.68. Found: N, 25.66; Cl, 25.41) and have obtained a product having properties similar to those reported for polyglycines.[1,2,3,4]

Treatment of an aqueous solution of 2 g. of (II) with sodium nitrite followed by the addition of dilute sodium hydroxide resulted in the formation of a precipitate which was washed with water and dried; yield, 0.83 g. (*Anal.* Found: C, 38.89; H, 5.47; N, 23.14). This white powder was insoluble in water and most organic solvents, but dissolved in concentrated hydrochloric acid and in strong alkali. The peptide nature of the compound was demonstrated by hydrolysis of 203 mg. of the substance with concentrated hydrochloric acid followed by benzoylation, yielding 500 mg. of recrystallized hippuric acid, m. p. 186–188° (*Anal.* Calcd. for $C_9H_9O_3N$: N, 7.82. Found: N, 8.18). The infrared absorption spectrum[5] further substantiated this conclusion. The formation of polymers by the interaction of (II) with nitrous acid may be considered to occur according to the following scheme, with triglycine azide hydrochloride (III) as an intermediate.

$$\mathrm{HCl\cdot H_2N{-}(R){-}CONHNH_2\cdot HCl}$$
$$\downarrow \mathrm{NaONO}$$
$$\mathrm{HCl\cdot H_2N{-}(R){-}CON_3} + \mathrm{NaCl} + \mathrm{H_2O}$$
$$\text{(III)}$$
$$\downarrow \mathrm{NaOH}$$
$$\mathrm{H_2N{-}(R){-}CON_3} + \mathrm{NaCl} + \mathrm{H_2O}$$
$$\downarrow \mathrm{H_2N{-}(R){-}CON_3}$$
$$\mathrm{H_2N{-}(R){-}CO{-}NH{-}(R){-}CON_3} + \mathrm{N_3H}$$
$$\downarrow \mathrm{H_2N{-}(R){-}CON_3}$$
$$\mathrm{H_2N{-}(R){-}CO{-}NH{-}(R){-}CO{-}NH{-}(R){-}CON_3} + \mathrm{N_3H}$$
$$\text{etc.}$$

This indicates that under our experimental conditions the rate of reaction of the hydrazide group in (II) with nitrous acid greatly exceeds the rate of deamination of the amino group, leading to the formation of (III) which undergoes polymerization as soon as the amino group is liberated by the addition of alkali.

Although the high insolubility of the product has precluded the determination of its molecular weight, the available evidence indicates strongly that the product represents a polyglycine (or a mixture of polyglycines). The application of this scheme to the polymerization of more complex tripeptides is under investigation.

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(1) Meyer and Go, *Helv. Chim. Acta*, **17**, 1488 (1934).
(2) Pacsu and Wilson, *J. Org. Chem.*, **7**, 117 (1942).
(3) Frankel and Katchalski, THIS JOURNAL, **64**, 2268 (1942).
(4) Mellon, Korn and Hoover, *ibid.*, **70**, 3040 (1948).
(5) We are indebted to Dr. Foil A. Miller of the Mellon Institute for the infrared absorption curves, which will be published later.

MASS SPECTROMETRIC EXAMINATION OF THE ISOMERIZATION OF *n*-PROPYL CHLORIDE

Sir:

The products of the isomerization of *n*-propyl chloride on aluminum chloride in the presence of deuterium chloride have been examined with a mass spectrometer to obtain further information about the mechanism of the rearrangement. If, as frequently postulated,[1] the isomerization occurs by elimination of hydrogen chloride and recombination according to Markownikoff's rule, a reasonable concentration of deuterium would be expected in the isopropyl chloride. Since no deuterium was found in the product, the experiments described here seem to establish the fact that the rearrangement at low temperatures (0°) does not proceed to any appreciable extent by the elimination of hydrogen chloride: $CH_3CH_2CH_2Cl \rightleftarrows CH_3CH{=}CH_2 + HCl \rightleftarrows CH_3CHCl{-}CH_3$.

The experiments were carried out in 150-cc. reaction vessels into which about 0.1 g. of aluminum chloride had been sublimed. Mixtures containing 5 cm. each of deuterium chloride or hydrogen chloride and *n*-propyl chloride were allowed to react at 0°. Samples were withdrawn at suitable time intervals for analysis with a Nier type mass spectrometer. Similar experiments were carried out in which propene was allowed to react with hydrogen chloride or deuterium chloride under the same conditions.

The mass spectral data summarized in Table I show that, after one hour at 0° when isomerization was practically complete, no deuterium was found in the isopropyl chloride. Under these same conditions and on the same catalyst deuterium chloride added to propene to give isopropyl chloride containing deuterium (compare masses 64, 66, 79 and 81).

The extent of the isomerization in a given length of time (60 to 70% in five minutes at 0°) was not appreciably changed by the presence of an equal pressure of either hydrogen chloride or deuterium chloride. This is further indication that hydrogen chloride is probably not involved in the rate-controlling process of the isomerization. The hydrochlorination of propene occurred under the same conditions but at an appreciably slower rate (10 to 20% in five minutes at 0°) with some polymerization. With an equal molar mixture of hydrogen chloride and deuterium chloride, the hydrogen chloride added to propene 2.2 times faster than did deuterium chloride.

In view of the result of the above experiments some other mechanism must be involved, possibly the formation of a carbonium ion,[2] or its equivalent, followed by an intramolecular hydride ion shift and recombination with a chloride ion of the catalyst. Additional exchange reactions are being

(1) Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941.
(2) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 320.

TABLE I

PARTIAL MASS SPECTRA OF REACTION PRODUCTS

No.	Gas sample	Catalyst	M./e. 27	63	64	65	66	78	79	80	81
1	n-C_3H_7Cl	None	100	21	1.0	6.2	...	4.8	..	1.2	...
2	i-C_3H_7Cl	None	100	62	3.3	19	0.5	20	0.5	5.4	...
3	n-C_3H_7Cl + DCl	I($AlCl_3$)	100	61	3.2	20	...	20	0.5	5.4	...
4[a]	C_3H_6 + DCl	I($AlCl_3$)	100	52	30	17	8.3	6.5	17	2.2	4.9
5	n-C_3H_7Cl + HCl	II($AlCl_3$)	100	62	3.5	20	...	21	0.6	6.0	...
6[a]	C_3H_6 + HCl	II($AlCl_3$)	100	55	3.0	16	...	22	0.7	4.2	...

[a] The isopropyl chloride was separated from these reaction mixtures for analysis.

used to investigate more fully these rearrangements.

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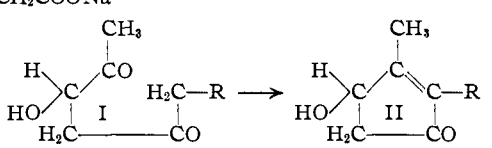
THE SYNTHESIS OF CYCLOPENTENOLONES OF THE TYPE OF CINEROLONE

Sir:

Henze[1] has studied 3-hydroxy-2,5-hexanedione and 2-hydroxy-1-phenyl-1,4-pentanedione. Hunsdiecker[2] has shown that aliphatic 1,4-diketones cyclize to cyclopentenones only if a $-CH_2-$ group is present in position 5.

We have prepared six hydroxy diketones of formula I by the reaction of pyruvaldehyde with aqueous solutions of alkali salts of beta-keto acids[3] at room temperature and about pH 8, under what may be considered "biological" conditions. On completion of the reaction, the products are extracted and distilled (60–75% yields). We have found that these hydroxydiketones could be cyclized to the cyclopentenolones of formula II by agitation with aqueous alkali (usually 2%) at room temperature, the products being then extracted and distilled (50–65% yields).

CH_3COCHO + RCH_2COCH_2COONa ⟶



(a) R = $-n$-C_4H_9; (b) R = $-CH_2CH{=}CHCH_3$; (c) R = $-CH_2CH{=}CH_2$; (d) R = $-CH_2C(CH_3){=}CH_2$; (e) R = $-CH_2CH_2CH{=}CH_2$; (f) R = $-CH_2CH{=}C(CH_3)_2$.

Hydroxydiketones[4]: Ia, $C_{10}H_{18}O_3$ 1.4514, 64.48, 9.74, 64.10, 9.56; Ib, $C_{10}H_{16}O_3$, 1.4679, 65.19, 8.76, 64.75, 8.79; Ic, $C_9H_{14}O_3$, 1.4657, 63.51, 8.29, 62.82, 8.05; Id, $C_{10}H_{16}O_3$, 1.4687, 65.19, 8.76, 65.28, 8.38; Ie, $C_{10}H_{16}O_3$, 1.4675, 65.19, 8.76, 65.01, 8.52; if, $C_{11}H_{18}O_3$, 1.4715, 66.64, 9.15, 66.80 8.75.

Cyclopentenolones[4]: IIa, $C_{10}H_{16}O_2$, 1.4945, 71.39, 9.59, 71.10, 9.64; IIb, $C_{10}H_{14}O_2$, 1.5143, 72.26, 8.49, 71.75, 8.40; IIc, $C_9H_{12}O_2$, 1.5141, 71.02, 7.95, 70.23, 8.07; IId, $C_{10}H_{14}O_2$, 1.5120, 72.26, 8.49, 72.48, 8.18; IIe, $C_{10}H_{14}O_2$, 1.5089, 72.26, 8.49, 71.88, 8.35, IIf, $C_{11}H_{16}O_2$, 1.5100, 73.29, 8.95, 73.44, 8.71.

Compound IIb, although having the same structure, is not identical with natural *dl*-cinerolone. However, its dihydro derivative is identical with compound IIa, and with *dl*-dihydrocinerolone. A similar lack of identity of synthetic 2-(2-butenyl)-3-methyl-2-cyclopenten-1-one with *dl*-cinerone has been reported[5] and attributed to geometric isomerism in the side chain.

The cyclopentenolones of formula II have been acylated with natural *d*-chrysanthemum monocarboxylic acid, and IIc with the *dl-cis-trans* synthetic acid, to furnish esters analogous to cinerin I.

All of these, except the ester of IIa, exhibit high toxicity and knockdown to flies, those of IIc and IId exceeding the "pyrethrins" in toxicity. These synthetic esters are more stable than the pyrethrins and cause no irritation when applied as sprays or aerosols.

The above synthesis of cyclopentenolones opens the way to the technical production of esters of the pyrethrin type since the synthesis of chrysanthemum monocarboxylic acid has been improved[6] and a more suitable substitute for this acid may yet be discovered.

Details of this research will be published later.

(1) Henze and co-workers, *Z. physiol. Chem.*, **189**, 121 (1930); **200**, 101 (1931); **214**, 281 (1933); and other references.

(2) Hunsdiecker, *Ber.*, **75B**, 455 (1942).

(3) Salts of beta-keto acids were prepared by cold saponification of beta-keto esters made according to the general procedure of Soloway and La Forge, THIS JOURNAL, **69**, 2677 (1947), and Green and La Forge, *ibid.*, **70**, 2287 (1948).

(4) Order of data for each compound: formula, $n^{25}D$, % C calcd., % H calcd., % C found, % H found.

(5) Harper, *J. Chem. Soc.*, 892 (1946).

(6) Campbell and Harper, *J. Chem. Soc.*, 283 (1945).

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THE INHOMOGENEITY OF HEPARIN

Sir:

It has been generally conceded that even highly purified heparin is non-homogeneous.[1] By

(1) R. Jensen, O. Snellman and B. Sylvén, *J. Biol. Chem.*, **174**, 265 (1948); J. E. Jorpes and S. Gardell, *ibid.*, **176**, 267 (1948); M. L. Wolfrom and R. A. H. Rice, THIS JOURNAL, **69**, 2918 (1947).