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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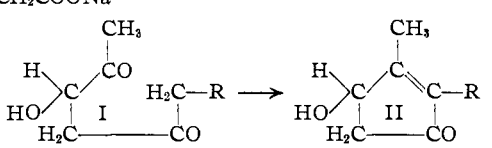
THE SYNTHESIS OF CYCLOPENTENOLONES OF THE TYPE OF CINEROLONE

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).