

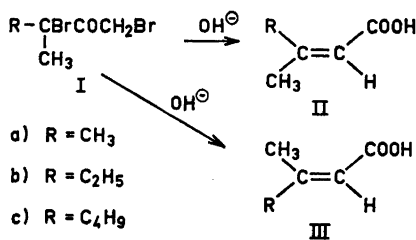
Favorsky Rearrangements

VIII. The Rearrangement of
1,3-Dibromo-3-methyl-2-onesCHRISTOFFER RAPPE and
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In connection with studies on the Favorsky rearrangement of dibromoketones^{1,2} it became of interest to study the rearrangement of 1,3-dibromo-3-methylpentanone-2 (I b) and 1,3-dibromo-3-methylheptanone-2 (I c).

The rearrangements of 1,3-dibromocompounds of methyl ketones unbranched at the α -carbon have been found to have geometric specificity. When alkali carbonates or bicarbonates were used as bases, *cis*-2-enoic acids could be obtained in good yields.^{1,2}

The rearrangement of I b has previously been studied by Wagner and Moore.³ As a basic reagent they used sodium methoxide in dry ether and they isolated 51 % of an ester fraction consisting of ester II b (57 %) and of III b (43 %), separated by distillation.



In this investigation other bases were used for the rearrangement. The products were isolated as an ether extract, and the determinations of the composition of the product were made by NMR. It was found from the NMR-spectra of β -chlorocrotonic and isocrotonic acid⁴ and 3,3-dimethylacrylic acid⁵ that a methyl group *cis* to a carboxyl has about 0.25 ppm higher δ -value than a methyl group *trans* to a carboxyl. The acids II and III each have one CH_3 -singlet which were used for the determination. In the crude extracts the singlets were 0.26 ppm apart. The yields

of crude extracts and the composition of these are given in Table 1. Due to disturbing groups in the background the determination of II c and III c was not as precise.

Table 1.

Dibromo- ketone	Base	Time h	Yield %	Composition	
				II %	III %
I a	KHCO_3	4	18	—	—
»	KOH	1/4	22	—	—
»	KOH ^a	1/2	28 ^b	—	—
»	NaOH	1/2	27	—	—
I b	KHCO_3	2	28	52	48
»	KOH	1	50	54	46
»	NaOH	1/4	51	55	55
I c	NaOH	24	65	50	50

^a solvent ethanol^b m.p. 60–63°C

In Table 1 are given the yields of the rearrangement of 1,3-dibromo-3-methylbutanone-2. From this dibromoketone, Wagner and Moore³ reported a yield of 58 % of the methyl ester of 3,3-dimethylacrylic acid using sodium methoxide in ether. Using alcoholic potassium hydroxide Favorsky and Wanscheidt obtained 3,3-dimethylacrylic acid, but they gave no yield for the rearrangement.⁶

An examination of the table shows that no geometric specificity was obtained in this rearrangement. The amounts of the *cis* and *trans* isomers in the crude extracts were about the same.

As pointed out by Kende the choice of bases has a strong affect on the yield.⁷ For example, contrary to the unbranched 1,3-dibromoketones,^{1,2} tri-,⁸ and tetrabromoketones,⁹ stronger bases such as alkali hydroxides give better yields in the present case than weaker bases like alkali carbonates and bicarbonates. Wagner and Moore found the same behaviour for 1-(bromoacetyl)-1-bromocyclohexane.^{3,10} It is worth noting that in the present investigation sodium salts gave somewhat higher yields than the potassium salts.

Experimental. The NMR-spectra were recorded on a Varian model A-60 spectrometer. *Preparation of dibromoketones.* *General procedure.* One mole of ketone was mixed with 100 ml 48 % hydrobromic acid and chilled to 0°C with ice-water. Bromine was added dropwise

(2.0 moles) and after 400 ml of water was added, the heavier organic layer was separated and it was immediately fractionated under reduced pressure.

1,3-Dibromo-3-methylbutanone-2, yield 56 %, b.p. 91–93°C/11 mm, $n_D^{25} = 1.5166$. Wagner and Moore gave no yield, b.p. 111°C/15 mm, $n_D^{20} = 1.5178$.³

1,3-Dibromo-3-methylpentanone-2, yield 67%, b.p. 114–115°C/10 mm, $n_D^{25} = 1.5146$. Wagner and Moore gave no yield, b.p. 57°C/1 mm, $n_D^{20} = 1.5155$.³

1,3-Dibromo-3-methylheptanone-2, yield 40%, b.p. 124–127°C/11 mm, $n_D^{25} = 1.5022$. (Found: C 33.63; H 4.94; Br 55.31. Calc. for $C_8H_{14}Br_2O$: C 33.59; H 4.93; Br 55.88).

Rearrangement of dibromoketone. General procedure. To 0.1 mole of dibromoketone was added a solution of 0.8 mole of the required hydroxide in 1000 ml of water or ethanol, 0.4 mole of the carbonate, or 0.8 mole of the bicarbonate in 1000 ml of water. The mixture was thoroughly stirred and when constant titration-values against methylorange were obtained (0.2 equiv. of base consumed), the solution was extracted with ether (3 × 100 ml), acidified with hydrochloric acid and again extracted with ether (5 × 100 ml). After drying, the ether phase was evaporated *in vacuo*. The yields and composition of the crude extracts are given in Table 1.

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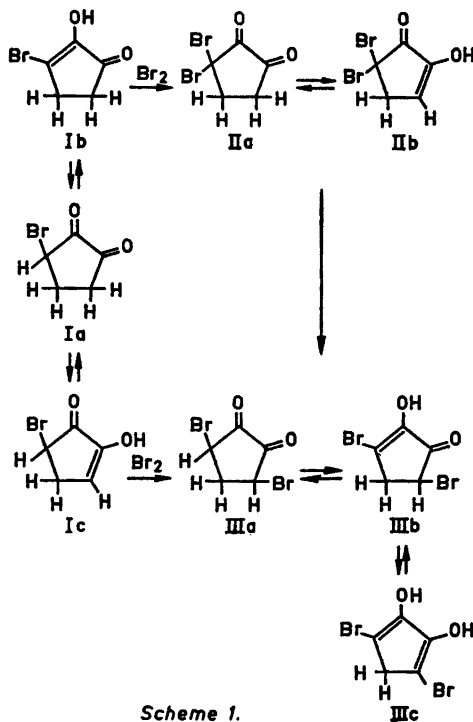
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The Bromination of 3-Bromocyclopentane-1,2-dione

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The bromination of ketones is presumed to proceed *via* the enol form.¹ 3-Bromocyclopentane-1,2-dione (Ia) is an interesting model substance for bromination studies since it already exists in its enol form, Ib.² From this enol the bromination should give 3,3-dibromocyclopentane-1,2-dione (IIa) or its enol form, IIb. From the other enol of 3-bromocyclopentane-1,2-dione (Ic) 3,5-dibromocyclopentane-1,2-dione (IIIa) or its enol form IIIb or IIIc would be formed, see Scheme 1.



Bromine was found to react easily with 3-bromocyclopentane-1,2-dione (Ib). From the reaction mixture a dibromoketone, $C_5H_6Br_2O_2$, could be isolated in 70 %