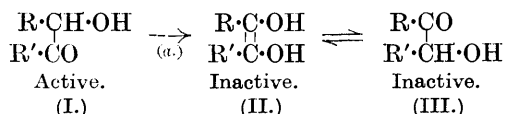


378. *The Interconversion of Mixed Benzoins.*

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CATALYTIC racemisation of esters, acid amides, etc., by means of alcoholic alkali has been extensively investigated by McKenzie and his collaborators, who have provided evidence that unsaturated substances are produced as intermediate phases. Wren (J., 1909, 95, 1593), for instance, found that if (–)benzoin was boiled for $\frac{1}{2}$ hr. with alcoholic potash, the recovered benzoin was optically inactive, and he considered that the racemisation took place through the intermediate formation of ω -dihydroxystilbene ($R = R' = Ph$) :



Since (–)benzoin does not undergo autoracemisation, it appears that the alcoholic alkali increases the velocity of the reaction (a). McKenzie, Roger, and Wills (J., 1926, 779) have shown, however, that the racemisation of (–)benzoin can be effected by means much less drastic than those employed by Wren, a trace of alcoholic potash causing almost complete racemisation in 24 hrs. in the cold.

Treatment of a mixed benzoin of the type $\text{CHR}(\text{OH}) \cdot \text{COR}'$ with alcoholic alkali would thus, probably, give rise to the intermediate phase $\text{CR}(\text{OH}) \cdot \text{CR}' \cdot \text{OH}$, which might then be transformed into a mixture of the isomerides $\text{CHR}(\text{OH}) \cdot \text{COR}'$ and $\text{CHR}'(\text{OH}) \cdot \text{COR}$, and the proportion in which they could be isolated by crystallisation of the mixture would depend largely on their relative solubilities. It is now shown that the transformation of a mixed benzoin into its isomeride can actually be realised.

When an ethyl-alcoholic solution of *r*-4'-methoxybenzoin (I; $R = \text{C}_6\text{H}_4 \cdot \text{OMe}$, $R' = \text{Ph}$) (McKenzie and Luis, *Ber.*, 1932, 65, 794) was treated at room temperature with alcoholic potash, *r*-4-methoxybenzoin (III; $R = \text{C}_6\text{H}_4 \cdot \text{OMe}$, $R' = \text{Ph}$) (McKenzie, Luis, Tiffeneau, and Weill, *Bull. Soc. chim.*, 1929, 45, 414) separated. This transformation may be represented as taking place through the formation of the unstable intermediate phase (as II). On similar treatment, the compound (III; $R = \text{C}_6\text{H}_4 \cdot \text{OMe}$, $R' = \text{Ph}$) was recovered unchanged from the solution. The latter result is not surprising since, from the condensation of benzaldehyde and anisaldehyde (McK., L., T., and W., *loc. cit.*) by potassium cyanide in ethyl-alcoholic solution, (III; $R = \text{C}_6\text{H}_4 \cdot \text{OMe}$, $R' = \text{Ph}$) was isolated.

When treated as described above, *r*-4'-dimethylaminobenzoin

(I; $R = C_6H_4 \cdot NMe_2$, $R' = Ph$) (McK. and L., *loc. cit.*) was partially transformed into its isomeride, *r*-4-dimethylaminobenzoin (as III) (Staudinger, *Ber.*, 1913, **46**, 3535; cf. Jenkins, Bigelow, and Buck, *J. Amer. Chem. Soc.*, 1930, **52**, 5198), together with some *p*-dimethylaminobenzil, $COPh \cdot CO \cdot C_6H_4 \cdot NMe_2$ (Staudinger, *loc. cit.*), which was isolated from the solution. When *r*-4-dimethylaminobenzoin was similarly treated, it crystallised from the solution together with the diketone. Moreover, it is (III; $R = C_6H_4 \cdot NMe_2$, $R' = Ph$) which is produced when benzaldehyde and *p*-dimethylaminobenzaldehyde are condensed in ethyl-alcoholic solution in the presence of potassium cyanide (J., B., and B., *loc. cit.*). The dimethylaminobenzoins differ from other benzoins in the readiness with which they undergo oxidation in the presence of alcoholic potash. Klinger (*Ber.*, 1886, **19**, 1862) obtained benzoic acid as one of the products when benzoin was heated with alcoholic potash in the presence of air, and the intermediate formation of benzil was assumed (cf., also, Knoevenagel and Arndts, *Ber.*, 1902, **35**, 1982; Jena and Limpricht, *Annalen*, 1870, **155**, 89); Tiffeneau and Lévy (*Compt. rend.*, 1931, **192**, 287; *Bull. Soc. chim.*, 1931, **49**, 725), however, heated a number of mixed benzoins with alcoholic potash and identified the acids formed in the decompositions, but in no instance did they record the isolation of the corresponding benzils or benzoic acids. (I; $R = C_6H_4 \cdot NMe_2$, $R' = Ph$) has now been heated with alcoholic potash, and the products identified were (III; $R = C_6H_4 \cdot NMe_2$, $R' = Ph$), *p*-dimethylaminobenzil, benzoic acid, and *p*-dimethylaminobenzoic acid. On similar treatment, (III) yielded the same products. When heating was prolonged, none of the diketone was isolated, and no evidence was obtained of the presence of *p*-dimethylaminobenzoic acid (Singh, J., 1925, **127**, 2445). This acid is, however, unstable, and has not been prepared by the action of alcoholic potash on *p*-dimethylaminobenzil.

It is clear from the above results that the method occasionally employed of determining the structure of ketones by scission by means of alcoholic potash, and identifying the products, is not applicable to mixed benzoins.

Jenkins (*J. Amer. Chem. Soc.*, 1931, **53**, 3115) noted that α -*p*'-chloro-*p*-dimethylaminobenzoin, $NMe_2 \cdot C_6H_4 \cdot CH(OH) \cdot CO \cdot C_6H_4Cl$, readily changes into the β -form, $C_6H_4Cl \cdot CH(OH) \cdot CO \cdot C_6H_4 \cdot NMe_2$, when heated with alcoholic potassium cyanide. (The latter mixed benzoin is formed by the condensation of *p*-dimethylaminobenzaldehyde and *p*-chlorobenzaldehyde in the presence of potassium cyanide.) This transformation is doubtless due to the presence of alcoholic potash, and if so, would fall into line with the results described in this paper.

EXPERIMENTAL.

Transformation of r-4'-Methoxybenzoin into r-4-Methoxybenzoin.—Alc. KOH (0.5 c.c.; 2.5%) was added to a solution of 0.5 g. of *r-4'*-methoxybenzoin, m. p. 100—101° (McK. and L., *loc. cit.*), in EtOH (12 c.c.). After 3 days at room temp., 0.35 g. of colourless crystals was deposited, which formed needles, m. p. 105.5—106.5°, from EtOH. The m. p. was not depressed on admixture with *r-4*-methoxybenzoin (McK., L., T., and W., *loc. cit.*) but was markedly depressed on admixture with the initial *r-4'*-methoxybenzoin. When a trace of the *r-4*-methoxybenzoin, obtained as above, was added to cold conc. H₂SO₄, a pale yellow colour developed slowly and changed gradually to an intense green. On warming, the green colour developed rapidly. *r-4*-Methoxybenzoin, prepared by the condensation of benzaldehyde and anisaldehyde, gives, however, a pink coloration with cold conc. H₂SO₄ if crystn. is not exhaustive; but after 15 crystns. from EtOH a specimen of this mixed benzoin (which had previously melted sharply and given correct results on analysis) gave no pink coloration with cold conc. H₂SO₄, but gave the coloration described above. The pink colour was due to a mere trace of anisoin. A trace of the latter (prep. by the method of van Alphen, *Rec. trav. chim.*, 1929, 48, 1112) gave with cold conc. H₂SO₄ an intense magenta coloration which faded to pale pink on warming. The coloration described by Rossel for anisoin (*Annalen*, 1869, 151, 33) is different from this. With cold conc. H₂SO₄ the colorations of *r-4*-methoxybenzoin and *r-4'*-methoxybenzoin are different: the latter gives an immediate yellow coloration which intensifies on standing or on warming.

In another expt., under different conditions, 3 c.c. of aq. KOH (10%) were added to a soln. of *r-4'*-methoxybenzoin (0.6 g.) in EtOH (15 c.c.). After 4 days at room temp., a cryst. solid was obtained which, when recryst. from EtOH, formed needles (0.2 g.), m. p. 105.5—106.5°, not depressed on admixture with authentic *r-4*-methoxybenzoin.

Action of Alcoholic Potassium Hydroxide on r-4-Methoxybenzoin.—When *r-4*-methoxybenzoin, m. p. 105.5—106.5°, was acted on by alc. KOH under conditions similar to those adopted for its isomeride, unchanged material separated.

Action of Alcoholic Potassium Hydroxide on r-4-Dimethylaminobenzoin.—2 C.c. of alc. KOH (20%) were added to a soln. of the mixed benzoin (1 g.), m. p. 162—163°, in EtOH (140 c.c.). After 18 days at room temp. a small crop of bright yellow solid, m. p. 112—115°, separated. Water was added to the filtrate, and the resulting yellow solid (0.3 g.) was crystallised from EtOH, giving bright yellow rhombic prisms, m. p. 115—116° (Found: C, 75.9; H, 6.0. Calc. for C₁₆H₁₅O₂N: C, 75.9; H, 6.0%), unaltered on admixture with *p*-dimethylaminobenzil (Staudinger, *loc. cit.*). The filtrate yielded a further 0.4 g. of solid from which unchanged *r-4*-dimethylaminobenzoin was isolated by crystn. from EtOH. The filtrate was carefully neutralised by HCl, and the small amount of solid which separated was crystallised from EtOH, affording needles, m. p. 234—235°, not depressed on admixture with *p*-dimethylaminobenzoic acid (Meisenheimer, *Annalen*, 1921, 423, 88).

In another expt., a conc. aq. soln. of KOH (8 g.) was added to *r-4*-dimethylaminobenzoin (4 g.) in EtOH (80 c.c.). After refluxing for 2 hrs. and standing over-night, the solution deposited 3 g. of a yellow solid which was triturated with C₆H₆ and then crystallised from EtOH; yield 0.9 g. of unchanged mixed benzoin. From the C₆H₆ soln., *p*-dimethylaminobenzil was isolated. To the

alkaline mother-liquor, H_2O (30 c.c.) was added and the EtOH expelled. The aq. soln. was extracted with Et_2O , and the extract yielded a small amount of the diketone. The aq. soln. was acidified by HCl, and Et_2O extraction afforded needles (0.2 g.), m. p. 119—120° (identified as benzoic acid). The acid soln. from which this acid had been extracted was carefully neutralised by NH_4OH and extracted with Et_2O ; the resulting needles, m. p. 234—235°, were identified as *p*-dimethylaminobenzoic acid.

Transformation of r-4'-Dimethylaminobenzoin into r-4-Dimethylaminobenzoin.—1 C.c. of alc. KOH (0.25%) was added to a solution of *r-4'*-dimethylaminobenzoin, m. p. 157—158° (0.5 g.), in EtOH (50 c.c.). After 2 days at room temp., yellow crystals (0.2 g.) were deposited. These were triturated with C_6H_6 and then crystallised from EtOH; colourless needles (0.1 g.), m. p. 161—162°, separated. The m. p. was not depressed on admixture with *r-4*-dimethylaminobenzoin, but was markedly depressed on admixture with the original mixed benzoin. The product was sparingly sol. in cold dil. HCl, in which *r-4'*-dimethylaminobenzoin is very readily sol. A trace of the product gave with cold conc. H_2SO_4 a bluish purple coloration, changing to orange-brown on warming (characteristic for *r-4*-dimethylaminobenzoin). *r-4'*-Dimethylaminobenzoin gives with cold conc. H_2SO_4 a pink coloration, changing to yellow-brown on warming.

The C_6H_6 soln. from which the *r-4*-dimethylaminobenzoin had been separated was evaporated to dryness, and from the residue *p*-dimethylaminobenzil was isolated by crystn. from EtOH.

In another expt., a solution of conc. aq. KOH (8 g.) was added to *r-4'*-dimethylaminobenzoin (4 g.) in EtOH (80 c.c.), and refluxed for 2 hrs. 30 C.c. of H_2O were added and the EtOH expelled. A yellow solid (3 g.) separated, and from it *r-4*-dimethylaminobenzoin and *p*-dimethylaminobenzil were isolated as in the previous expt. Again, both benzoic and *p*-dimethylaminobenzoic acids were isolated by treating the alk. solution as already described.

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