[Contribution from the Chemical Laboratory of the University of Illinois]

A New Synthesis of Mixed Benzoins. Second Paper

By Richard T. Arnold[1] and Reynold C. Fuson

The new synthesis of mixed benzoins by the condensation of suitable aromatic compounds with arylglyoxals[2] has been extended to a number of new cases, and has been found to be generally useful in the preparation of this type of substance. In Table I are listed the various benzoins which have been made, together with indications as to the conditions employed.

Preparation of the Arylglyoxals

The glyoxals were prepared in good yields by the method of Riley and Gray,[3] with an added modification as follows.

After the oxidation with selenium dioxide, the dioxane solution is decanted from the precipitated selenium and distilled under atmospheric pressure until nearly all of the dioxane has passed over. At this point, 100 cc. of a suitable hydrocarbon[4] is added, and the solution again distilled at atmospheric pressure until the distillate is no longer turbid. At this stage, the solution is transferred to a Claisen flask, and the distillation completed under diminished pressure. This modification was employed to prevent the formation of the glyoxal hydrate which normally contaminates the distillate. By use of this method with commercial xylene (b. p. 137–140°), *p*-bromophenylglyoxal (b. p. 115° (7 mm.); m. p. 51–52°), and *p*-chlorophenylglyoxal (b. p. 123–125° (17 mm.); m. p. 40–42°) were prepared in 64 and 55% yields, respectively. These compounds were identified by conversion into their hydrates which melted at 132°[13] and 121°, respectively.

Preparation of the Benzoins

The optimum conditions for this reaction are typified in the synthesis of *p*-bromobenzoin.

Table I

Benzoin	M. p., °C.	Yield, %	Time, hrs.	Solvent	Analyses, % Calcd.		Analyses, % Found		Diketone
					C	H	C	H	
$C_6H_5COC(OH)HC_6H_5$	133	90	20	C_6H_6					95°
$(CH_3)_3C_6H_2COC(OH)HC_6H_2(CH_3)_3$[5]	59- 60	48	15	CS_2	81.08	8.18	80.84	8.051	118–119[6]
$C_6H_5COC(OH)HC_6H_4OCH_3$	100[7]	48	5	CS_2					62- 63[7]
$C_6H_5COC(OH)HC_{10}H_7$	128	42	15	CS_2	82.4	5.4	82.3	5.7	87[8]
$C_6H_5COC(OH)HC_6H_4Cl$	116[11]	84	15	CS_2					73[10]
$ClC_6H_4COC(OH)HC_6H_5$	90–91[11]	35	15	C_6H_6					73[10]
$C_6H_5COC(OH)HC_6H_2(CH_3)_3$	93.5–94[12]	62	5	CS_2	80.3	7.14	80.0	7.4	134–136[2]
$(CH_3)_3C_6H_2COC(OH)HC_6H_5$	102–103[2]	63	7	C_6H_6					134–136[2]
$BrC_6H_4COC(OH)HC_6H_5$	108–109	70	15	C_6H_6	57.73	3.78	57.62	3.81	84- 85[10]
$C_6H_5COC(OH)HC_6H_4Br$	125–126	57	15	C_6H_5Br	57.73	3.78	57.93	3.94	84- 85[10]
$C_6H_5COC(OH)HC_6H_4CH_3$	116[11]	50	15	CS_2					31[10]
$CH_3C_6H_4COC(OH)HC_6H_5$	110[11]	42	15	CS_2					31[10]

Ten and sixty-five hundredths grams of *p*-bromophenylglyoxal was dissolved in 50 cc. of benzene and placed in a 125-cc. separatory funnel.

In a 500-cc., three-necked, round-bottomed flask surrounded with ice and equipped with a mercury-sealed stirrer were placed 200 cc. of dry benzene and 13.3 g. of aluminum chloride. The glyoxal solution was added dropwise to the benzene–aluminum chloride solution. The addition took approximately thirty minutes. The reaction was allowed to run at 0° for fifteen hours. The reaction mixture was then decomposed by adding slowly ice-cold 20% hydrochloric acid solution. The benzene solution was concentrated by removal of the solvent under diminished pressure. The process was performed in the absence of air,

---

[1] Chemical Foundation Fellow in Organic Chemistry, 1935–1936.

[2] Fuson, Weinstock and Ullyot, This Journal, **57**, 1803 (1935).

[3] Riley and Gray, "Organic Syntheses," Vol. XV, John Wiley and Sons, New York, 1935, p. 67.

[4] For this purpose, the hydrocarbon should have a boiling point about 10–15° above the melting point of the glyoxal hydrate.

[5] Zinc chloride was used instead of aluminum chloride for a catalyst.

[6] Kohler and Baltzly, This Journal, **54**, 4015 (1932).

[7] McKenzie and Luis, *Ber.*, **65B**, 794 (1932).

[8] This benzil is new. *Anal.* Calcd. for $C_{18}H_{12}O_2$: C, 83.09; H, 4.63. Found: C, 82.93, 82.87; H, 4.73, 4.74.

[9] Jenkins, This Journal, **56**, 682 (1934).

[10] Hatt, Pilgrim and Hurran, *J. Chem. Soc.*, 93 (1936).

[11] Weissberger, *Ann.*, **478**, 112 (1934).

[12] Weinstock and Fuson, This Journal, **58**, 1233 (1936).

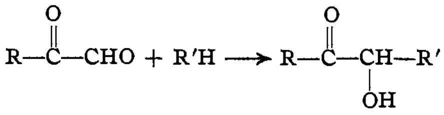
[13] Söderbaum, *Ber.*, **26**, Ref., 1015 (1893).

and was continued until the residual solution was reduced to a volume of 30 cc. To this was added 30 cc. of low-boiling petroleum ether, and the solution kept cold overnight. The precipitate was separated by filtration with suction and washed with four 25-cc. portions of cold, low-boiling petroleum ether. The material weighed 10.2 g. (70.2% of the theoretical amount), and melted at 105–106°. After one recrystallization from ethyl alcohol, the benzoin melted at 108–109°.

The general procedure involves the use of the hydrocarbon reactant as the solvent; in some cases, however, carbon disulfide has been found to give very satisfactory results.

The Structure of the Benzoin

In every case where the resulting benzoin is known, our product showed perfect agreement with the published descriptions of the compound anticipated. In cases where both benzoin isomers were prepared, both were oxidized by iodine[14] to give identical diketones. Most of these diketones are known substances.[10] It is important to note that in each instance only one benzoin was obtained, and that in every case the structure of the benzoin corresponded to that to be expected on the basis of the general equation



$$R-\overset{O}{\overset{\|}{C}}-CHO + R'H \longrightarrow R-\overset{O}{\overset{\|}{C}}-\underset{OH}{\underset{|}{CH}}-R'$$

Summary

Twelve benzoins have been prepared by condensation of arylglyoxals with aromatic hydrocarbons or their derivatives. The structures of the mixed benzoins have been shown to be those which would be predicted on the basis of the general equation as indicated above.

[14] Carson and McAllister, THIS JOURNAL, **51**, 2822 (1929).

URBANA, ILLINOIS RECEIVED MAY 25, 1936

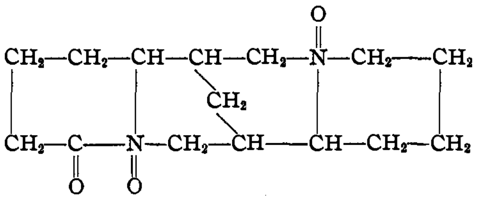
[CONTRIBUTION FROM THE PATHOLOGICAL DIVISION, BUREAU OF ANIMAL INDUSTRY]

Lupine Studies. XI. The Alkaloids of *Lupinus Barbiger* S. Wats.

BY JAMES FITTON COUCH

In a previous communication[1] the occurrence of sparteine in *Lupinus barbiger* was announced. At that time the presence of two other alkaloids of undetermined identity was indicated. This paper describes the isolation and identification of these alkaloids. *L. barbiger* is a perennial species ranging from Colorado, Utah, Arizona, and California.[2] Two lots of material, one from northern Arizona and one from Utah were examined in the course of this study and no significant differences between them were found.

Three well-defined alkaloids were isolated from this species: sparteine and two hitherto undescribed bases which have been named dilupine and trilupine. Lupinine and lupanine were sought for and found not to be present. The new alkaloids are of unusual interest. Trilupine, $C_{15}H_{24}O_3N_2$, proved to be an amine oxide derived from *d*-lupanine of which it is the di-N-oxide corresponding to the structure



By the action of hydrogen dioxide on sparteine the di-N-oxide of that base has been prepared[3] by a number of workers. Polonovski[4] has shown that geneserine is the amine oxide of eserine and analogous compounds have been prepared synthetically from other bases.[5] This is, however, the first instance in which amine oxides have been discovered in a lupine species. It was found that while gold chloride and platinum chloride would yield the corresponding double salts of trilupine if the mixtures were not heated for more than a short time, other acids and longer heating resulted

---

[1] J. F. Couch, THIS JOURNAL, **54**, 1691 (1932).

[2] W. W. Eggleston, in I. Tidestrom, "Flora of Utah and Nevada," *Contr. U. S. Nat. Herbarium*, **25**, 297 (1925), Govt. Printing Office, Washington.

[3] F. B. Ahrens, *Ber.*, **20**, 2218 (1887); Wackernagel and Wolffenstein, *ibid.*, **37**, 2220 (1904); A. Valeur and E. Luce, *Compt. rend.*, **168**, 1276 (1919).

[4] Max Polonovski, *Bull. soc. chim.*, **21**, 191 (1917).

[5] (a) Max and Michel Polonovski, *Compt. rend.* **180**, 1755 (1925); (b) M. Freund and E. Speyer, *Ber.*, **43**, 3310 (1910); (c) R. Wolffenstein, *ibid.*, **25**, 2777 (1892).