Fig. 4 for different fibers in the dry state and in Fig. 5 for the same fibers in the swollen state.

When the curves are straight lines, this would highly support (although not fully prove) the conclusion of independent scattering by the particles[3]; but this is seldom the case, as Warren and Biscoe[4] for example pointed out in their experiments on carbon black.

The curves of Fig. 4 show that in the case of dry fibers no straight lines are ever obtained. The curves obtained with swollen fibers (Fig. 5), on the other hand, differ from those of dry fibers by being perfectly straight as would be the case when the above assumptions are fulfilled.

The conclusion, therefore, is obvious that due to the swelling process, the particles are so far moved apart that inter-particle interference no longer plays a part, and the calculation of the particle size from the slope of the curves appears permissible. Another important conclusion from the straight shape of the curve is that the size of the particles will not vary to a large extent around an average value.

In Table I the slopes of the curves obtained with different fibers following this new swelling technique are given; these values are proportional to the sizes of the particles in the different fibers, indicating their ratios.

TABLE I

Fiber	Slope	Radius of gyration, Å.		Diameter, Å.	
		a	*b*	*a*	*b*
Jute	218	9.50	7.75	26.87	21.92
Hydrolyzed jute	296	11.07	9.03	31.32	25.54
Flax	313	11.39	9.29	32.21	26.27
Rayon (viscose)	396	12.81	10.45	36.23	29.55
Rayon (fiber G)	396	12.81	10.45	36.23	29.55
Rayon (fortisan)	450	13.65	11.14	38.62	31.50
Ramie	540	14.95	12.20	42.31	34.51

Values for radii of gyration are given in two columns in Table I, one using formula (a) and the other formula (b). The values of the particle diameter given also in Table I were calculated from the two sets of radii of gyration but under the assumption that the particles in both cases have the shape of an elongated cylinder.

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(3) If the various assumptions are fulfilled on which Guinier's theory is based, including independent scattering, the theory requires these curves to be straight lines.

(4) J. Biscoe and B. E. Warren, *J. Applied Phys.*, **13**, 364–371 (1942).

SCHOOL OF TEXTILES
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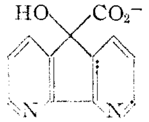
RECEIVED AUGUST 4, 1950

The Loss of Carbon Monoxide from 1,2-Diketones

BY P. H. GORE AND G. K. HUGHES

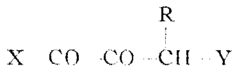
In a recent communication, G. E. Inglett and G. F. Smith[1] have recorded the formation in almost quantitative yield of 4,5-diazafluoren-9-one by alkaline treatment of 1,10-phenanthroline-5,6-quinone.

They regarded this removal of the elements of carbon monoxide as a "very surprising development," yet the reaction is perfectly analogous to the benzilic acid-type rearrangement[2] of phenanthrene-5,6-quinone, which with fairly concentrated alkali gives 9-hydroxy-9-carboxyfluorene[3] and with more dilute alkali fluoren-9-one.[4] The intermediate formation of 9-hydroxy-9-carboxy-4,5-diazofluorene followed by removal of formate ions thus provides an explanation.



Inglett and Smith further state that this is "the first reaction in which carbon monoxide has been observed to be lost from a 1,2-diketone grouping." However, several 1,2-diketones have long been known to lose carbon monoxide by the action of heat: diethyl 3,4-diketoadipate (ketipinic ester), 2,4,5,7-tetraketoöctane, 1,6-diphenyl-1,3,4,6-tetraketohexane and 1,4-diphenyl-1,4-dicyano-2,3-diketobutane.[5]

It appears from this, and from work carried out in this Laboratory, that for loss of carbon monoxide to occur at temperatures below about 160° (for 2-keto esters) or 250° (for 1,2-diketones), the following grouping should be present, both in 2-keto esters and in 1,2-diketones



$$X\ \ CO-CO-\overset{\displaystyle R}{\overset{|}{C}H}-Y$$

where

X = CHCOR' or OR'
R = H, alkyl or aryl
Y = electron-attracting group

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(1) G. E. Inglett and G. F. Smith, THIS JOURNAL, **72**, 842 (1950).

(2) J. Liebig, *Ann.*, **25**, 27 (1838); N. Zinin, *ibid.*, **31**, 329 (1839); M. Bösler, *Ber.*, **14**, 323 (1881); L. Gattermann, *Ann.*, **347**, 364 (1906); etc.

(3) A. Baeyer, *Ber.*, **10**, 125 (1877); P. Friedländer, *ibid.*, **10**, 534 (1877).

(4) R. Anschütz and F. R. Japp, *ibid.*, 11, 211 (1878).

(5) W. Wislicenus, *ibid.*, **28**, 811 (1895).

SCHOOL OF CHEMISTRY
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RECEIVED JUNE 9, 1950

4,4'-Difluorobenzhydrol

BY F. A. GUNTHER AND R. C. BLINN

The authors recently reported[1] the synthesis of 4,4'-difluorobenzhydrol, a compound previously unrecorded in the literature, along with its simple properties and some of its reactions. In February, 1950, Picard and Kearns reported[2] the synthesis of the same compound by a different series of reactions. Whereas our benzhydrol melted at 47.3–47.5°, theirs melted at 92–93°. Rigid comparisons of the two compounds indicate different structures.

In our hands reduction of 4,4'-difluorobenzophenone with zinc and alkali gave the desired benzhydrol (II), whereas attempted reductions by aluminum isopropoxide yielded an unidentified substance (V) in the hands of Picard and Kearns The reaction schemes are as follows:

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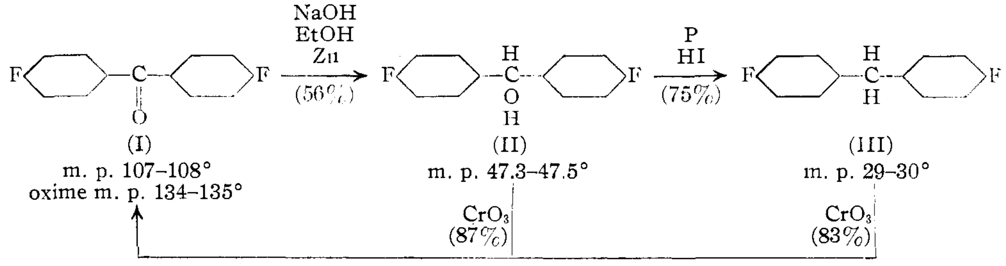
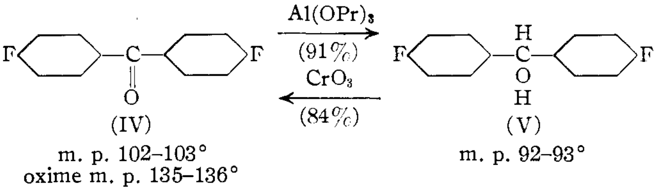
(1) F. A. Gunther and R. C. Blinn THIS JOURNAL, **72**, 4282 (1950).

(2) Picard and Kearns, *Can. J. Research*, **28B**, 56 (1950).

Gunther and Blinn



Picard and Kearns



Compounds I and IV are identical, as shown by mixed melting points, and by comparisons of their oximes and 2,4-dinitrophenylhydrazones.

The analytical comparisons carried out in these laboratories are summarized in Table I.

TABLE I

ANALYTICAL COMPARISONS OF COMPOUNDS IN SYNTHETIC SCHEMES

Compound	Source^a	Mol. wt. Calcd.	Mol. wt. Found	Analyses, % Carbon Calcd.	Analyses, % Carbon Found	Analyses, % Hydrogen Calcd.	Analyses, % Hydrogen Found
I	G & B	218	220	71.96	...	3.93	..
I 2,4-dinitrophenylhydrazone	G & B	397	407	...	...	..	..
II	G & B	220	218	70.90	70.58	4.52	4.58
II *p*-nitrobenzoate	G & B	369	368	65.03	65.16	3.55	4.00
III	G & B	204	206	76.46	76.90	4.94	5.19
III 3,3′-dinitroderivative	G & B	...	...	53.07	53.26	2.74	2.94
IV	P & K						
	G & B	...	...	71.96	...	3.93	..
V	P & K^b	220	361	70.90	73.57	4.52	4.72

^{a} As prepared by Gunther and Blinn (G & B) or by Picard and Kearns (P & K). ^{b} As prepared by P & K, but recrystallized and analyzed by G & B from sample obtained from Dr. Picard.

Compounds II (b. p. 150–154° (5 mm.)) and V (b. p. 143° (3 mm.)) exhibit depressed melting points in admixture. They are probably not dimorphic since supercooling the melts of each and cross seeding did not effect conversion of one to the other. Their ultraviolet absorption characteristics are shown in Table II.

TABLE II

ABSORPTION CHARACTERISTICS

Compound	EtOH λ min.	ε	EtOH λ max.	ε	EtOH λ min.	ε	EtOH λ max.	ε
II	239	202	265	1431	269	868	271	1211
V	241	367	265	1352	269	867	271	1234
II + V^a	240	367	265	1463	269	900	271	1266

^{a} II = 45.3%, V = 54.7%.

Solvation phenomena are eliminated from consideration by the fact that both compounds II and V retain essentially the same melting points after repeated meltings, after recrystallizations from a variety of solvents, and after prolonged drying at reduced pressures over desiccants.

It has not been possible to apply the existing data for compound V to any reasonable structures of possible products from the treatment of 4,4′-difluorobenzophenone with aluminum isopropoxide.[3]

It would ordinarily be anticipated that the aluminum isopropoxide reduction of the ketone would proceed normally, with greater chances for stray reactions with a zinc and alkali reduction. Hence, the results obtained are puzzling. The claim of Picard and Kearns is, nevertheless, in error, and the substance supposed by them to be the substituted benzhydrol was not completely characterized and in fact does not even show the required analysis for this substance. The data summarized here do support the assigned structure of our compound II as 4,4′-difluorobenzhydrol.

Experimental.—The reactions diagrammed and sources of parent ketones are presented and discussed in the literature cited, with two exceptions. The conversions of II and III to I and of V to IV were accomplished in the yields shown with the aid of chromic anhydride in acetic acid, in the usual manner. All other comparison data were obtained with accepted procedures. Melting points are uncorrected.

[3] See Wilds, "Organic Reactions," Vol. II, John Wiley & Sons, Inc., New York, N. Y., pp. 178–223.

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The Preparation and Properties of 5-Ethyl-5-(1-methyl-1-nitroethyl)-barbituric Acid

BY E. B. HODGE

The preparation of ethyl ethyl-(1-methyl-1-nitroethyl)-malonate has recently been reported.[1] Since it seems that there is no record of the hyp-

[1] E. E. Van Tamelen and G. Van Zyl, THIS JOURNAL, **71**, 835 (1949). Since this note was written, the preparation of 5-methyl-5-(1-methyl-1-nitroethyl)-barbituric acid has been reported: E. E. Van Tamelen and G. Van Zyl, *ibid.*, **72**, 2979 (1950).