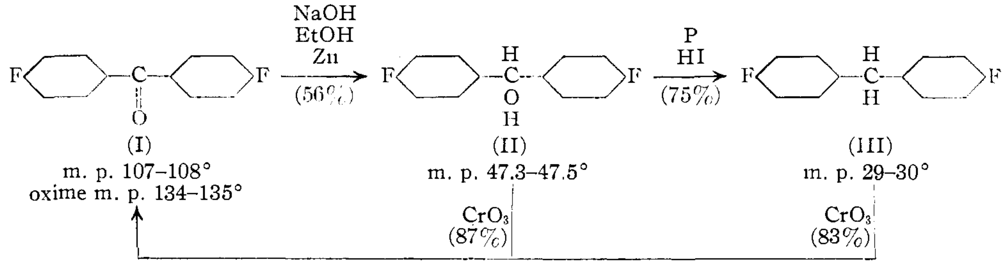
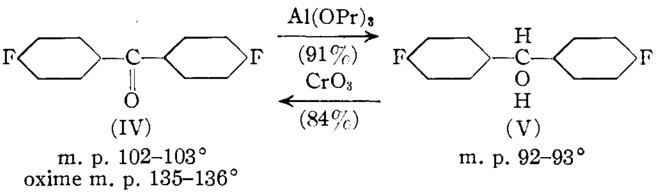
Gunther and Blinn



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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RECEIVED JUNE 5, 1950

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-

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[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).

notic properties of a barbituric acid with a 5-alkyl substituent containing a nitro group, it was thought to be of interest to prepare the barbituric acid from the above compound.

Considerable difficulty was experienced in bringing about the condensation between urea and ethyl ethyl-(1-methyl-1-nitroethyl)-malonate. The desired compound was finally obtained in 9% yield using a modification of a procedure described by McElvain and Goese.[2]

The pharmacological properties of the sodium salt of the compound were studied by Dr. J. N. Spencer of the Pharmacology Department of this Laboratory. He reports the following properties.

Intraperitoneal LD_{50} (mice)	360 mg./kg.
Oral LD_{50} (mice)	490 mg./kg.
Hypnotic dose (ED_{50}) (intraperitoneal in mice)	110 mg./kg.
No hypnotic action observed following oral administration in mice.	

Experimental

5-Ethyl-5-(1-methyl-1-nitroethyl)-barbituric Acid.—To a mixture of 4.8 g. (0.08 mole) of urea, 11 g. (0.04 mole) of ethyl ethyl-(1-methyl-1-nitroethyl)-malonate, and 100 ml. of dry *t*-butyl alcohol was added 0.5 g. of sodium methoxide. The alcohol was distilled from the stirred mixture at about 30 ml. per hour and fresh *t*-butyl alcohol was added continuously at the same rate. One-half gram portions of sodium methoxide were added every hour until 3.5 g. had been added. One hour after the last portion of sodium methoxide had been added, the *t*-butyl alcohol was distilled under reduced pressure. The residue was cooled, 100 ml. of water was added, and, after a short period of stirring, the water was extracted with 50 ml. of ether. Acidification of the water with concd. hydrochloric acid gave 0.9 g. of white ppt., m. p. 233–237°. Recrystallization from ethanol raised the m. p. (cor.) to 238–240° (dec.).

Anal. Calcd. for $C_9H_{13}N_3O_5$: C, 44.44; H, 5.39; N, 17.27. Found: C, 44.55; H, 5.46; N, 17.00.

McElvain and Goese[2] had used sodium *t*-butoxide as a catalyst. In the reaction reported the more readily available sodium methoxide was found to give equally good results.

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(2) S. M. McElvain and M. A. Goese, THIS JOURNAL, **65**, 2226 (1943).

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The Resonance Energy of Benzene

BY DONALD F. HORNIG

Only a small displacement of the carbon atoms is necessary to distort a normal benzene molecule with 1.39 Å. C–C bonds to a configuration where C–C bonds are alternately 1.34 and 1.54 Å.; *i.e.*, the configuration represented by a single Kekulé structure without resonance. Since the displacements are small, the energy expended in distorting the molecule can be obtained from the force constants derived from the vibrational spectrum. If, as is sometimes assumed, the bond length is a sufficient criterion of bond type, this energy might be expected to equal the resonance energy.

Since the C–H distance and H–C–C angle of Kekulé benzene are the same as those of benzene, the distortion involves only the two symmetry coordinates[1]

$$S_1 = (1/\sqrt{6})(r_1 + r_2 + r_3 + r_4 + r_5 + r_6)$$
$$S_{14} = (1/\sqrt{6})(r_1 - r_2 + r_3 - r_4 + r_5 - r_6)$$

whose forms are illustrated in Fig. 1. The r's are the changes in the C–C bond lengths. The force constants corresponding to these symmetry coordinates have been designated Λ_1 and Λ_2 by Crawford and Miller[1] who found that $\Lambda_1 = 7.83 \times 10^5$ dyne/cm. Inserting the frequencies of the B_{2u} vibrations obtained by Mair and Hornig[2] (Table I) into the equations of Crawford and Miller, two possible sets of force constants for the B_{2u} species are obtained. They are given in Table II.

TABLE I

FREQUENCY OF B_{2u} VIBRATIONS IN BENZENE

Compound	ν_{14}, cm.$^{-1}$	ν_{15}, cm.$^{-1}$
C_6H_6	1311	1147
C_6D_6	1287	825

TABLE II

B_{2u} FORCE CONSTANTS

	Force constant $\times$ 10^5 dyne/cm.	
C–H bending, Γ_2	0.828	0.828
C–C stretching, Λ_2	4.361	3.926
Interaction, μ_2	0.667	0.290

The C–H bending force constant, Γ_2, is essentially identical with those obtained for other symmetry species by Crawford and Miller, 0.83, 0.87 and 0.85 × 10^5 dynes/cm., agreeing better than the value 0.95 × 10^5 dynes/cm. obtained by them for the B_{2u} species, using the earlier frequency assignment of Ingold and co-workers.[3] It is difficult to choose between the alternative values for Λ_2 or μ_2 on physical grounds but fortunately they are so nearly the same that the choice does not affect the conclusions markedly. Both values of Λ_2 are surprisingly low, lower than expected even for single bonds. However, since a force constant represents the curvature in the potential energy function in the vicinity of the equilibrium configuration, it is reasonable to expect that when relatively stable configurations with only slight differences in geometry exist (the Kekulé forms in this case) the potential energy will change slowly, giving rise to an abnormally low force constant. This may also be the reason for the abnormally low force constants found for the central C–C bonds in diacetylene, for example.[4]

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(1) B. L. Crawford, Jr., and F. A. Miller, *J. Chem. Phys.*, **17**, 249 (1949).

(2) R. D. Mair and D. F. Hornig, *ibid.*, **17**, 1236 (1949).

(3) N. Herzfeld, C. K. Ingold and H. G. Poole, *J. Chem. Soc.*, 222 (1946).

(4) See G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York, N. Y., 1945, p. 323.