trans-dihydro compound[7,13–15] (*cis*-**6** and *trans*-**6**). If J_{cis} were significantly different from J_{trans}, then in the nmr spectrum of **6** each isomer should have two doublets distinguishable from those of the other isomer. However, the nmr spectrum of **6** exhibited (along with an acid proton at δ 12.05) only two sharp doublets centered at δ 3.73 and 2.58 with $J = 8.3$ Hz.[16] Thus, J_{cis} and J_{trans} were not significantly different.

The coupling constants for **5** and for **6** were slightly different (0.3 Hz). This observation has the following implications. In our sample of **6**, one isomer (either *cis* or *trans*) predominated whose coupling constant was 8.3 Hz. The other isomer, in order to average out J_{app} in **5** to be 8.6 Hz in an ABX system, must have $J = 8.9$ Hz. Thus, the J_{cis}/J_{trans} ratio (either 8.3/8.9 = 0.93 or 8.9/8.3 = 1.07) would be very close to unity.

If the puckering in **5** were intermediate between that in **1** and **2**, one would expect the J_{cis}/J_{trans} ratio for **5** to be between that of **1** and **2**. However, the ratio for **5** lies outside this range and is less than that for **1**. It is difficult to believe that **5** is *less* puckered than **1**. Instead, it is to be concluded that the J_{cis}/J_{trans} ratio is only a rough approximation of the degree of puckering, and that **1** and **5** are puckered to about the same extent. Since **5** would be expected to be puckered (*vide supra*), it would seem that 1,4-cyclohexadiene (**1**) is definitely in a boat conformation and that a single moderately sized substituent can be fitted into this conformation comfortably in the pseudo-equatorial position.

Experimental Section

Melting points were determined by a Thomas-Hoover melting point apparatus. Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer and a Varian HA-100 spectrometer, using tetramethylsilane as the internal standard. Ultraviolet spectra were recorded on a Beckman DB spectrophotometer.

1,4-Dihydrobenzoic Acid (5).—This compound was prepared from benzoic acid by the procedure of Kuehne and Lambert[13] and was transparent in the region of 240–270 mμ, indicating the absence of the 1,3-cyclohexadiene chromophore.

Benzoic Acid-d_5.—Reaction of bromobenzene-d_5 (Stohler Isotope Chemicals, Azusa, Calif.) with magnesium and subsequent carbonation with Dry Ice[17] gave benzoic acid-d_5 in a 50% yield, mp (H_2O) 119–121°. An nmr spectrum of the product exhibited no signals in the aromatic region.

2,3,4,5,6-Pentadeuterio-1,4-dihydrobenzoic Acid (6).—Birch reduction of benzoic acid-d_5 in the usual manner[13] gave an 82% yield of **6**, bp 77–79° (0.4 mm).

Registry No.—**5**, 4794-04-1.

Acknowledgment.—Acknowledgment is made to the Research Corporation (Frederick Gardner Cottrell Grant-in-Aid), to the Robert A. Welch Foundation, Grant No. B-325, and to North Texas State University for a Faculty Research Grant for support of this work.

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[13] M. E. Kuehne and B. F. Lambert, *Org. Syn.*, **43**, 22 (1963).

[14] G. W. Brown and F. Sondheimer, *J. Amer. Chem. Soc.*, **89**, 7116 (1967).

[15] R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *ibid.*, **91**, 4535 (1969).

[16] Owing to the small extent of aliphatic–olefinic coupling in **5**, D–H coupling in **6** was negligible and deuterium decoupling was not necessary.

[17] H. Gilman, N. B. St. John, and F. Schulze, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 425. Our procedure is different from that of Gilman in that the Grignard reaction mixture was poured over Dry Ice instead of bubbling in gaseous carbon dioxide.

Electronic and Nuclear Magnetic Resonance Spectra of Dithizone

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Several metal complexes of dithizone (1,5-diphenylthiocarbazone) are photochromic when irradiated with visible light.[1] During a study of this photochromic system,[2] we became interested in the electronic spectra and photochromism of dithizone itself.

When dissolved in methylene chloride, dithizone forms an intense green solution having the spectrum shown by the solid line in Figure 1. Intense irradiation of the green solution with visible light, in *dry*, nonpolar solvents, produces a red, metastable form (dashed line in Figure 1) which returns very rapidly to the original green.[3] The orange, nonphotochromic dithizonate anion produced in alkaline solution is shown by the dotted line in Figure 1.

It is unusual for a neutral molecule of this size to possess the intense, low-energy absorption (molar absorptivity ≅ 37,000 at 6100 Å) shown by the long-wavelength band of the green form. No comparable band exists for the oxygen analog of dithizone (diphenylcarbazone) which is orange in neutral solution because of a weak $n \rightarrow \pi^*$ transition appearing as a shoulder on intense ultraviolet $\pi \rightarrow \pi^*$ transitions.

The relative intensities and λ_{max} values for the two visible bands in the dithizone spectrum depend upon the solvent, and some workers[4] have interpreted these changes to indicate that the two bands originate from a thiol–thione tautomeric system. Although we have observed such solvent effects, we have been unable to interpret them rigorously, since they appear to be complicated by acid–base equilibria, trace metal effects, and even oxidative decomposition of the dithizone.

We could not obtain the nmr spectrum of dithizone itself because of poor solubility, but we have obtained the spectrum of an alkylated derivative [1,5-di(*o*-ethylphenyl)thiocarbazone] in $CDCl_3$. The chemical shifts (τ values referred to TMS, Varian A-60) were −2.03 (1.6 protons), 1.9 and 2.67 (8 aromatic), 7.0 (4 methylene), and 8.6 (6 methyl). The signal at τ −2.03 showed no evidence of splitting over the temperature range +50 to −45° in $CHCl_3$ solution (in fact, the peak became somewhat narrower at lower temperatures) and disappeared upon addition of CH_3-OD.

We feel that these nmr results favor a single (equivalent proton) structure instead of rapid exchange between a form containing S–H and a form containing N–H. For the latter case we would expect splitting

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[1] L. S. Meriwether, E. C. Breitner, and C. L. Sloan, *J. Amer. Chem. Soc.*, **87**, 4441 (1965).

[2] R. A. Coleman, W. H. Foster, Jr., J. Kazan, and M. Mason, Final report, "Synthesis of Chromotropic Colorants," Feb 1966, U. S. Army Natick Laboratories, Natick, Mass., Contract No. DA19-129-AMC-269(N), issued as Technical Report 66-0-CM, Series TS-138, AD630908.

[3] The photochromism of dithizone was previously reported by Meriwether, *et al.*[1]

[4] P. S. Pel'kis and R. G. Dubenko, *Zh. Obshch. Khim.*, **29**, 194 (1959).

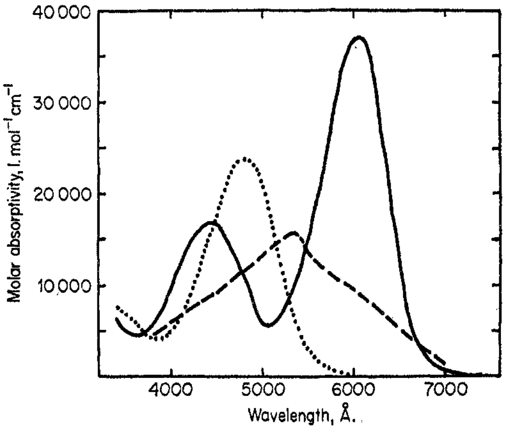
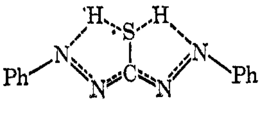


Figure 1.—Electronic spectra of three forms of diphenylthiocarbazone: ———, methylene chloride at room temperature; ······, alkaline methylene chloride–methanol at room temperature ($\sim$0.005 N NaOH in 95% (vol) methylene chloride–5% methanol); - - - - -, hexane at $\sim$1°, while irradiated with the full intensity of the near-infrared tungsten lamp in the Cary 14.

(or at least broadening) of the τ -2.03 peak at low temperature instead of the slight narrowing which was observed.

We propose structure **1** to represent the green form existing in neutral solutions of dithizone.



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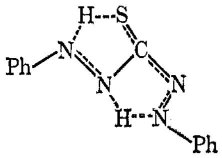

2

Structure **2**, which can be obtained by isomerization about a carbon–nitrogen double bond, may be responsible for the red, metastable form. The nmr spectrum of this form cannot be studied, since the incident light beam is completely absorbed at the surface of the concentrated solutions required for nmr. Consequently only a small fraction of the molecules is converted to the metastable form.

The exact explanation for the intensity of the long-wavelength peak in the spectrum of the green form is still lacking, but it appears unlikely that a simple thiol–thione tautomeric system can account for the spectrum.

Registry No.—Dithizone, 60-10-6.

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Reaction of Diazomethane with Some α,β-Unsaturated Acetals and Aldehydes

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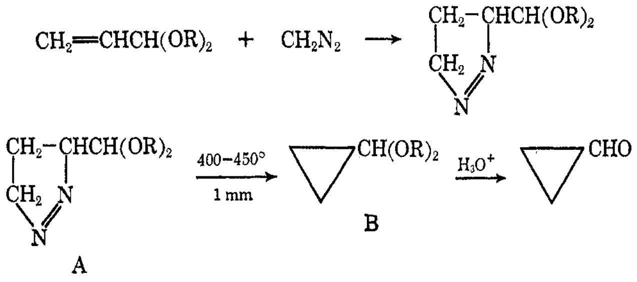
A fairly recent report[1] has described an improved method of synthesis of cyclopropanecarboxaldehyde by ceric nitrate oxidation of cyclopropylcarbinol. We wish to report a new synthesis of this aldehyde which represents at least a more economical method, since cyclopropylcarbinol is a relatively expensive starting material. This procedure involves a three-step sequence with various acrolein acetals as starting materials—each step being accomplished in good to excellent yields. Acrolein acetals, including the cyclic 2-vinyl-1,3-dioxolanes and 2-vinyl-1,3-dioxanes, can be obtained commerically or may be conveniently prepared from acrolein.[2] Reaction of diazomethane with the unsaturated acetal forms a 1-pyrazoline. This can be readily pyrolyzed to the corresponding acetal of cyclopropane carboxaldehyde, which is then hydrolyzed to the aldehyde. Overall yields for the three steps ranged as high as 50%. Table I lists yields, physical constants, and elementary analytical data for compounds of types A and B as prepared from different acrolein acetals.



The pyrazolines obtained from all of the acrolein acetals used were of the indicated Δ^1 structure, as evidenced by the lack of an NH absorption band near 3400 cm^{-1} and the presence of an N=N absorption at 1540 cm^{-1} in the infrared spectra. The direction of addition of diazomethane to the double bond is assumed to be that demonstrated for alkene linkages having other adjacent electron-withdrawing groups.[3]

Vapor phase pyrolysis of the pyrazolines, following the method used by McGreer,[4] gave yields of 73–96%. These pyrazolines proved to be relatively more heat stable, and higher temperatures (400–450°) and lower pressure (1 mm) were necessary than for the conjugated pyrazolines pyrolyzed in McGreer's work. A number of unsuccessful attempts were made to photolyze these pyrazolines, using a 450-W Hanovia lamp.

The most difficult step for which to develop good yields proved to be the final hydrolysis. Use of inorganic acid solutions resulted in very poor yields. The best method developed during our study involved the use of a minimum amount of trichloroacetic acid to effect the water solution. With the cyclic acetals, yields of cyclopropanecarboxaldehyde were much better than with the diethyl acetal, owing to the difficulty of complete separation of ethanol from the aldehyde in the latter case.

An investigation was also made of the reaction of diazomethane with acrolein itself, in the hope of realizing a two-step synthesis of cyclopropanecarboxaldehyde. Although a rapid reaction occurred, it proved to be impossible to isolate the simple addition

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[1] L. B. Young and W. S. Trahanovsky, *J. Org. Chem.*, **32**, 2349 (1967).

[2] R. F. Fischer and C. W. Smith, *ibid.*, **25**, 319 (1960).

[3] R. Huisgen, R. Grashey and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, London, 1964, Chapter 11.

[4] D. E. McGreer, W. Wai, and G. Carmichael, *Can. J. Chem.*, **38**, 2410 (1960).