extracted with hot acetone until no more product was obtained. The combined acetone and chloroform solutions were evaporated to dryness, and after two crystallizations from ethyl acetate, 2.6 g. of 1,3-cyclopentanedione (36%) was obtained, m.p. 151.5–152.5°, $\lambda_{max}^{0.1N\ HCl}$ 242 mμ ε 20,000.

2,2-Dichloro-1,3-cyclopentanedione. To 1,3-cyclopentane dione (1 g., 0.01 mole) in a very small amount of dry benzene, was added slowly with stirring a slight excess of sulfuryl chloride (2.0 ml., 0.025 mole). As the reaction proceeded, more benzene was introduced, and when all the material had gone into solution, the benzene was evaporated and the remaining substance recrystallized twice from ether to give 1.34 g. of 2,2-dichloro-1,3-cyclopentanedione (80%), m.p. 83.5°, $\lambda_{max}^{95\%\ ethanol}$ 277 mμ, ε 160.

Anal. Calcd. for $C_5H_4O_2Cl_2$: C, 35.95; H, 2.41; Cl, 42.42. Found: C, 35.70; H, 2.44; Cl, 42.88.

2,2-Dichloro-cis-1,3-cyclopentanediol. 2,2-Dichloro-1,3-cyclopentanedione (100 mg., 0.6 mmole) was added with stirring to an ice-cooled solution of sodium borohydride (29 mg., 0.76 mmole) in water (5 ml.) and isopropyl alcohol (5 ml.). Water was added after 20 min.; the solution extracted with ether three times and the ether solution dried. The organic solvents were then evaporated, and the residue was recrystallized from chloroform to give a compound (75 mg., 75%), m.p. 135.5°, giving the correct analysis for 2,2-dichloro-1,3-cyclopentanediol.

Anal. Calcd. for $C_5H_8O_2Cl_2$: C, 35.17; H, 4.70; Cl, 41.43. Found: C, 35.58; H, 4.81; Cl, 41.08.

Although the infrared spectrum of this compound, $\lambda_{max}^{CHCl_3}$ 2.76, 3.41, 9.03, 9.90, 10.22, 11.31, 11.66 μ, was similar to caldariomycin, $\lambda_{max}^{CHCl_3}$ 2.74, 3.41, 8.97, 9.72, 10.29, 11.31., 12.00 μ, it was not identical.

2,2-Dichloro-trans-1,3-cyclopentanediol. In a three necked 50-ml. flask equipped with a reflux condenser, mechanical stirrer, and a flow of nitrogen gas was placed lithium aluminum hydride (550 mg., 15 mmoles) in ether (25 ml.). The mixture was brought to a temperature of −2° and maintained there while 2,2-dichloro-1,3-cyclopentanedione (1.5 g., 9 mmoles) in ether was added dropwise over a 0.5-hr. period. After the addition was completed, the reaction mixture was stirred for 10 more min., whereupon the contents of the flask were poured into ice-cold 2*N* hydrochloric acid (100 ml.). The acidic solution was extracted with seven equal volumes of ether. The ether solution was dried over magnesium sulfate and evaporated to dryness. Chloroform (6 ml.) was added to the solid material and the mixture heated until no more of the crystals went into solution. The chloroform solution was held at −20° for several hours for crystallization. The crystals were separated from the supernatant liquor and determined to be identical with the product of the sodium borohydride reduction (750 mg., 50%). When the mother liquor was evaporated down and the remaining crystals sublimed at 95° under reduced pressure (water aspirator), a compound (300 mg., 20%), m.p. 89–90°, was obtained giving the correct analysis for caldariomycin and exhibiting the identical infrared spectrum as the natural product.

Anal. Calcd. for $C_5H_8O_2Cl_2$: C, 35.17; H, 4.70; Cl, 41.43. Found: C, 35.58; H, 4.83; Cl, 41.10.

d-Camphor-10-sulfonyl chloride. *d*-Camphor-10-sulfonic acid (1 g., 0.43 mmole) was treated with thionyl chloride (1 ml., 1.4 mmoles) and heated at 60° until the reaction had stopped. The solution was then poured into water, and the solid material separated by centrifugation. The residue was recrystallized once from acetone-water to give 970 mg. (90%), m.p. 67–70°.

Caldariomycin-bis-d-camphor sulfonate. To a solution of caldariomycin (100 mg., 0.59 mmole) in anhydrous pyridine (0.5 ml.) in a 15-ml. glass centrifuge tube was added *d*-camphor-10-sulfonyl chloride (300 mg., 1.2 mmoles). The tube warmed immediately and a precipitate formed. After 5 min., excess 2*N* hydrochloric acid (5 ml.) was added; and the mixture vigorously stirred. The precipitate was obtained by centrifugation and dried overnight under reduced pressure over phosphorus pentoxide. A sample recrystallized from 95% ethanol melted at 142–143°, $[\alpha]_D^{25}$ +36° (acetone).

Anal. Calcd. for $C_{25}H_{36}O_8S_2Cl_2$: C, 50.08; H, 6.01; Cl, 11.85. Found: C, 50.14; H, 6.28; Cl, 12.08.

Reaction of D,L-*caldariomycin with d-camphor-10-sulfonyl chloride.* The synthetic D,L-caldariomycin (204 mg., 1.2 mmoles) was mixed with the *d*-camphor-10-sulfonyl chloride (620 mg., 2.4 mmoles) according to the procedure used for the natural material. A product was obtained (189 mg.), m.p. 125–135°, which, after 4 recrystallizations from acetone-water, melted at 138–142°, $[\alpha]_D^{25}$ +37°. Upon admixture of this material with the similar derivative of caldariomycin, no depression of the melting point was observed, m.p. 139–143°.

The infrared spectra of the dicamphor sulfonate derivatives of natural caldariomycin and the synthetic product were identical, $\lambda_{max}^{CHCl_3}$ 3.38, 5.73, 7.23, 8.48, 10.35, 11.22, 11.82 μ.

Attempted cleavage of caldariomycin–camphor sulfonate derivative. To a solution of lithium aluminum hydride (74 mg., 2 mmoles) in anhydrous chloroform (20 ml.) was added caldariomycinbis-*d*-camphor sulfonate (200 mg., 0.33 mmole) in anhydrous chloroform (20 ml.). The mixture was stirred for 1 hr. at 20° and then added carefully to water (50 ml.). The water layer was extracted several times with ether; the ether solutions washed once with water, dried over magnesium sulfate, and evaporated to dryness. The residue was redissolved in chloroform (0.5 ml.) and cooled to −20°. No caldariomycin appeared even upon seeding.

Cl^{36}-labeled caldariomycin. *Caldariomyces fumago* was grown on the Czapek-Dox medium described by Clutterbuck *et al.*[5] in the presence of potassium chloride[36] (10,000 c.p.m./μmole). Caldariomycin, labeled with Cl^{36}, was isolated as previously described.[5]

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The Effect of Ring Substituents on Prototropic Isomerism in Phenylhydrazones[1]

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The wide use of arylhydrazones as analytical derivatives of aldehydes and ketones for spectroscopic analysis necessitates an understanding of any changes in structure which may occur in solution. Any isomerization may require the reporting of a time factor for purposes of obtaining reproducible spectra of these derivatives.

Thus phenylhydrazones of aliphatic aldehydes and ketones have been shown[4] to exist originally as the hydrazone isomer (I) and to isomerize rapidly in solution to the more stable benzeneazoalkane (II).

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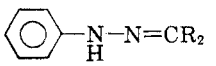
(4) R. O'Connor, *J. Org. Chem.*, 26, 4375 (1961).

TABLE I

ULTRAVIOLET AND VISIBLE SPECTRA
(Solvent: Absolute Methanol)

Compound	λ_{max}(mμ)	ϵ (Molar Extinction Coefficient)	λ_{max}(mμ)	ϵ
Butanone *N*-methyl-*p*-nitrophenylhydrazone	393	24,400	232	11,500
Butanone *p*-nitrophenylhydrazone	394	24,300	250	11,800
Butanone *N*-methyl-2,4-dinitrophenylhydrazone	379	16,800	224	15,500
Butanone 2,4-dinitrophenylhydrazone[a]	361	22,400		
Butanone phenylhydrazone[b]	270	18,400		
Butanone *p*-tolylhydrazone[c]	274	17,600		
2-Methyl-2-*p*-tolylazopropane	271	10,500	408	183
2-Phenylazobutane (in hexane)	265	8,000	401	130
2-*p*-Tolylazobutane	273	11,000	402	174
2-*p*-Tolylazobutane[d]	273	11,000	406	168

[a] Reported spectrum in chloroform: λ_{max} 365 mμ, ϵ 21,600 L. A. Jones and C. K. Hancock, *J. Org. Chem.*, **25**, 226 (1960). [b] In solution for 16 min. [c] In solution for 20 min. [d] In heptane solution. Tolylhydrazone solution was allowed to stand until λ_{max} at 406 mμ was constant. This required 70 min. at a concentration of $3 \times 10^{-3}M$.



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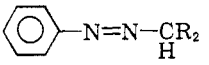

II

The effect of ring substituents on this isomerism has been reported for substances which may involve a quinoidal form.[5] The present study is an investigation of the relative stabilities of hydrazone and azo isomers of butanone arylhydrazones containing nitro or methyl ring substituents.

The *N*-methyl-*p*-nitrophenylhydrazone of butanone, prepared as a reference standard for the hydrazone form, showed infrared absorption characteristic of the phenyl group (1600 cm.$^{-1}$) and the C=N group (shoulder at 1640 cm.$^{-1}$).[6] The infrared spectrum of the *p*-nitrophenylhydrazone was nearly identical to that of the above cited reference compound except for N—H absorption at 3320 cm.$^{-1}$ Also nearly superposable were the ultraviolet and visible spectra (Table I), and these spectra did not change with time. Thus, a *p*-nitro substituent on the phenyl ring effectively prevents tautomerism of the arylhydrazone in neutral solution.

A considerable difference was noted in the spectra of the 2,4-dinitrophenylhydrazone of butanone and the *N*-methyl-2,4-dinitrophenylhydrazone (Table I), although both have the 1640-cm.$^{-1}$ infrared absorption characteristic of the C=N of the hydrazone form. The differences in their ultraviolet spectra may be due to different geometrical isomer distributions or, as has been suggested by Bohlmann,[7] hydrogen-bonding with the *ortho*-nitro group may account for these differences. The latter possibility is supported by infrared dilution studies of the N—H region.

The infrared spectrum of the *p*-tolylhydrazone of butanone is like that of the phenylhydrazone, showing N—H absorption at 3340 cm.$^{-1}$ and C=N absorption (shoulder at 1640 cm.$^{-1}$), and the ultraviolet spectra are essentially superposable (Table I). Comparison with the established structure[4] of the phenylhydrazone shows that the *p*-tolylhydrazone exists in fresh solution in the hydrazone form. The *p*-tolylhydrazone isomerized in solution to a benzene-azoalkane-type compound (Table I), which, when isolated by fractional distillation, was identical with 2-*p*-tolylazobutane, prepared by the method of Curtin and Ursprung.[8] That this product is an azo compound can be seen by comparison of its spectrum with that of 2-methyl-2-*p*-tolylazopropane (Table I). The isomerization of the *p*-tolylhydrazone is about one-tenth as rapid as that of the phenylhydrazone,[4] requiring seventy minutes for complete hydrazone-to-azo conversion in $10^{-3}M$ hexane solution.

A change in the spectra of the *p*-tolylazoalkanes on prolonged exposure to sunlight or fluorescent lighting appears to involve, as in the case of azobenzene,[9] a change in the geometrical isomer ratio.

The influence of the nitro group in stabilizing the hydrazone form and that of the methyl group in favoring isomerization to the azo form are consistent with the findings of Singu.[5] The stability of the *p*-tolylazoalkane is demonstrated by the absence of any spectral shift toward that of the hydrazone even after several months in solution.

Comparison of these results with the case of phenylhydrazone isomerism[4] indicates that arylhydrazones of other ketones and of aldehydes should behave in a similar manner. Thus, the reporting of spectra of arylhydrazones containing *o,p*-directing ring substituents should be accompanied by a statement of solvent and of time in solution in order to assure reproducible spectral data.

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EXPERIMENTAL

Infrared spectra. The infrared spectra were recorded with a Beckman IR-4 double-beam spectrophotometer. Liquids were run as films and the solids as chloroform or carbon tetrachloride solutions, as Nujol mulls, or as potassium bromide pellets.

Ultraviolet and visible spectra. The spectra were taken using a Beckman DK Recording Spectrophotometer or a Beckman DU Spectrophotometer. Solutions were of a concentration sufficient to obtain maximum optical density of 0.8 at the λ_{max}. For initial comparison spectra, all solutions were absolute methanol. Time stability studies were made with methanol or hexane solutions.

Preparation of hydrazones. Excess redistilled reagent grade butanone was refluxed for about 30 min. with the arylhydrazine. Excess butanone was removed by evaporation and the product, when solid, was recrystallized from ethanol to a constant melting range. Liquid hydrazones were distilled under reduced pressure until a product of constant refractive index was obtained.

Phenylhydrazine, N-methylphenylhydrazine, p-nitrophenylhydrazine, p-tolylhydrazine, and *2,4-dinitrophenylhydrazine.* These compounds were obtained from commercial sources and were purified by recrystallization or distillation.

N-Methyl-p-nitrophenylhydrazine. This was prepared by the method of Cuisa and Rastelli.[10] The product melted at 156–158° (reported[10] m.p. 156°).

N-methyl-2,4-dinitrophenylhydrazine. This hydrazine was synthesized by the method of Blanksma and Wackers[11]; m.p. 144–145° (reported[11] m.p. 144°.)

2-Phenylazobutane. A $3 \times 10^{-3}M$ solution of butanone phenylhydrazone in purified hexane was allowed to stand for 30 min. The azo compound formed was not isolated but its visible spectrum was recorded using the original solution and its ultraviolet spectrum was recorded using a solution made by diluting the original one-hundred fold.

2-Methyl-2-p-tolylazopropane. This azo compound was prepared from *t*-butylzinc chloride and *p*-toluenediazonium fluoborate by a method similar to that used by Curtin and Ursprung[8] for synthesis of benzeneazoalkanes. The yield of pure product was 19% (b.p. 90–93°/8 mm.; n_D^{22}, 1.5125).

Anal. Calcd. for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15; N, 15.89. Found: C, 74.86; H, 9.17; N, 16.01.

2-p-Tolylazobutane. This product was prepared by the same method as the 2-methyl-2-*p*-tolylazopropane, yield: 26%; b.p. 96–98°/7 mm.; $n_D^{25°}$, 1.5124.

Anal. Calcd. for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15; N, 15.89. Found: C, 74.77; H, 9.21; N, 15.96.

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(10) R. Cuisa and G. Rastelli, *Gazz. chim. ital.*, **52**, 126 (1922).

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Pyrolysis of *cis*- and *trans*-3-Hexenedioic Acids

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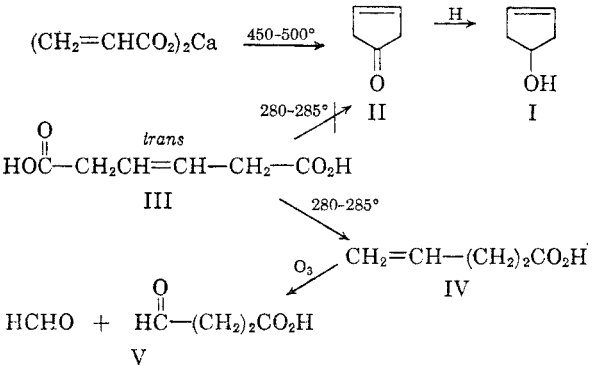
Certain projected syntheses in this laboratory required that we obtain reasonable quantities of 3-cyclopenten-1-ol (I) as an intermediate. Preparation of this cyclic alcohol has been reported by Winstein, *et al.*[1] *via* the hydroboronylation of cyclopentadiene, and by Alder and Flock[2] who reduced the corresponding unsaturated ketone with lithium aluminum hydride; the ketone II was obtained in poor yield by the pyrolysis of dieyclopentadienol-3.

Dashkevich[3] reported that the pyrolysis of calcium acrylate at 450–500° gave 3-cyclopenten-1-one (II) in about 27% yield. This appeared to offer many advantages for the preparation of reasonable quantities of an intermediate which could be converted readily to I. However, in repeated attempts to duplicate this pyrolysis, we were unable to obtain any detectable amount of ketone II.

The fact that certain aliphatic dibasic acids and their alkaline-earth metal salts readily undergo pyrolysis to form cyclic ketones suggested the possibility that the commercially available 3-hexenedioic acid (III) might also be cyclized to the ketone II. Pyrolysis of III at 280–285° yielded a liquid product which exhibited none of the properties reported for the ketone II. This pyrolysis product was found to be an unsaturated monobasic acid having an infrared absorption characteristic of a terminal olefin group. Since ozonolysis of the purified acid yielded both formaldehyde and β-formylpropionic acid (V), the liquid pyrolysis product from III is 4-pentenoic acid (IV).



The dimethyl ester of III, prepared by the action of ethereal diazomethane on a purified sample of III, showed an infrared absorption at 10.4 μ,

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