TABLE I

Compound	R	M. p., °C.	Yield, %[b]	Formula	Carbon, %[a] Calcd.	Carbon, %[a] Found	Hydrogen, % Calcd.	Hydrogen, % Found
I	*o*-NO_2	131–132	71	$C_{10}H_{10}N_2O_4$	54.05	54.22	4.54	4.62
	m-NO_2	142–143	72	$C_{10}H_{10}N_2O_4$	54.05	54.19	4.54	4.67
II	*o*-NO_2	126–127	81	$C_{11}H_{12}N_2O_5$	52.38	52.30	4.80	4.95
	m-NO_2	160–162	78	$C_{11}H_{12}N_2O_5$	52.38	52.48	4.80	5.03
III	*o*-NO_2	187–188	19	$C_{11}H_{14}N_2O_5$	51.96	51.98	5.55	5.69
	m-NO_2	172–173	28	$C_{11}H_{14}N_2O_5$	51.96	51.82	5.55	5.64
IV	*o*-NO_2	125–126	52	$C_{11}H_{12}Cl_2N_2O_5$	40.88	41.10	3.75	3.88
	m-NO_2	135–136	61	$C_{11}H_{12}Cl_2N_2O_5$	40.88	41.25	3.75	3.95

[a] Analytical data were determined by Mr. C. E. Childs of this Laboratory. [b] Yield of I is based on hexamethylenetetramine salt while yields of II, III and IV are based on the preceding intermediate.

The mixture was stirred and a solution of 1.2 g. of sodium bicarbonate and 0.4 g. of sodium carbonate in 20 ml. of water was added. After twenty minutes a clear solution was formed and within an additional twenty minutes a granular solid began to precipitate. The mixture was stirred for forty-five minutes and then cooled to 5°. The solid product was filtered off, washed thoroughly with water and dried. A sample was recrystallized from a mixture of benzene and isoöctane.

DL-*threo*-2-Acetamido-1-*o*-nitrophenyl-1,3-propanediol.—To a hot solution of 13.1 g. (0.064 mole) of aluminum isopropoxide in 110 ml. of anhydrous isopropyl alcohol was added 13.5 g. (0.053 mole) of α-acetamido-β-hydroxy-*o*-nitropropiophenone. The mixture was stirred and acetone was removed by means of a Hahn condenser over a period of two hours. A total of 70 ml. of isopropyl alcohol was removed by distillation. The residue was allowed to cool somewhat and 25 ml. of water was added. The mixture was refluxed for fifteen minutes and then filtered through a layer of Super-cel. The filter-cake was extracted twice with hot 50-ml. portions of 80% isopropyl alcohol. The extracts were combined and concentrated *in vacuo*. The residue was dissolved in a small quantity of ethyl acetate. On cooling the solution a crystalline product was obtained.

DL-*threo*-2-Dichloroacetamido-1-*o*-nitrophenyl-1,3-propanediol.—A mixture of 2.5 g. (0.01 mole) of DL-*threo*-2-acetamido-1-*o*-nitrophenyl-1,3-propanediol and 25 ml. of 5% hydrochloric acid was heated on a steam-bath with occasional swirling for one hour. The hot solution was charcoaled and filtered. The filtrate was cooled and made strongly basic with 20% aqueous sodium hydroxide. The resulting solution was extracted several times with small portions of ethyl acetate. The extracts were combined, dried over anhydrous magnesium sulfate and then concentrated *in vacuo*. The residue was mixed with 1.5 g. of methyl dichloroacetate in 7.5 ml. of methanol and refluxed for one hour. The solution was diluted with 25 ml. of ethylene dichloride and concentrated *in vacuo*. The residue, a colorless solid, was recrystallized from water.

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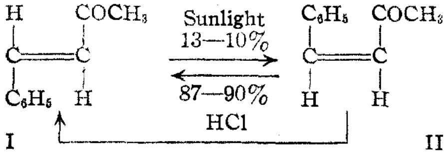
Spectroscopic Evidence for the Sunlight Conversion of *trans* to *cis*-Benzalacetone

BY ROBERT E. LUTZ, CARL R. BAUER[1] AND ROBERT H. JORDAN[2]

In an investigation stemming from the recent isolation of *cis*-benzalacetophenone[3] it has been possible to demonstrate the formation of a *cis*-isomer (II) upon exposure to bright sunlight of an isoöctane solution of ordinary (*trans*) benzalacetone (I). The optical density of the solution decreased rapidly to a quasi-equilibrium point without apparent change in λ_{max}, but beyond this point upon further exposure there occurred a continuing slow decrease in optical density which was evidence of other (permanent) transformations. The contribution to the optical density by the *cis* isomer and secondary transformation products, and the concentration of the *trans* isomer, were determined by measuring the optical density of the same solution after freezing out the bulk of the *trans* isomer to reduce concentration to a small and known value. It followed from the data obtained that the concentration of the *trans* isomer in the original solution after exposure to sunlight was 77% of the original, and that 23% had been converted into the *cis* isomer and other transformation products. The actuality of the presence of *cis*-benzalacetone in the solution after exposure to sunlight was demonstrated by the increase in optical density of this solution after treatment with hydrochloric acid according to the scheme used for converting *cis*- to *trans*-benzalacetophenone,[3] and, in the case of the solution from which the bulk of the *trans* isomer had been frozen out, by similar treatment with hydrochloric acid followed by freezing out and identification of the *trans* compound regenerated. These facts are consistent with the postulated *cis*–*trans* relationships but not with polymerization–depolymerization.



The best estimate of the actual ratio of *cis*-benzalacetone at photoequilibrium is 13% and the lowest 10%, and of the *trans* isomer 87–90%.

The absorption spectrum of the solution after exposure and removal of the bulk of the *trans*-benzalacetone showed only one measurable peak at 278 mμ, and a part of the absorption at this point is attributed to *cis*-benzalacetone. It appears that λ_{max} for the *cis* isomer is approximately the same as that of the *trans*. The molar extinc-

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(1) du Pont Co. Fellow, 1949–1950.

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(3) Lutz and Jordan, This Journal, 72, 4090 (1950).

tion coefficient is 6–8 × 10^3 with the likelihood that it is closer to the lower figure; this is in contrast to 22 × 10^3 at λ_{max} for the *trans* isomer. The simplest explanation for these facts is that in the *cis* isomer there is little steric interference with the conjugated system but that interference with planarity results in a serious diminution of the efficiency of absorption.[4]

Experimental

All primary solutions in the following were brought to the same dilution (1:10,000) in order to bring them into the range of the Beckman DU quartz spectrophotometer. Since a constant dilution factor was used, concentrations in grams per 100 ml. are referred for convenience directly to the optical density (D) of the dilute solution. Thus the factor 10,000 is canceled out automatically in the following discussion of results.

A solution of 1.039 g. of pure *trans*-benzalacetone (λ_{max} 278.0 mμ) in 100.0 ml. of isoöctane (0.0712 molar) was exposed for approximately 1.5 hours to bright winter sunlight. The initial optical density (D_1) was 0.150 at 278.0 mμ and the D_2 after exposure was 0.129. After removal of the excess *trans*-benzalacetone by chilling the solution to −24° the optical density (D_3) was 0.045. The solubility of pure *trans*-benzalacetone at −24° was found to be 0.148 molar by spectrophotometric measurement; this corresponds to an optical density of 0.031. Thus it is apparent that at 278.0 mμ the contribution (D_4) of the *cis*-benzalacetone and any secondary transformation products is 0.014 (D_3 minus 0.031).

For the unchilled exposed solution the contribution (D_5) of the *trans* isomer is 0.115 (D_2 minus D_4). This corresponds to a 0.0546 molar concentration of *trans*-benzalacetone in the exposed solution. The difference from the original concentration, 0.0166 mole per liter, represents the amount of *trans*-benzalacetone converted to the *cis* form and other transformation products.

A portion of the exposed solution with a drop of added concd. hydrochloric acid was refluxed for fifteen minutes, treated with excess solid sodium carbonate, and transferred quantitatively to a volumetric flask. Upon proper dilution the optical density (D_6) was found to be 0.142 at 278.0 mμ.

Assuming that the combined contributions of the *cis* isomer and other transformation products to this value is 0.014 or less (D_4), the contribution of the *trans* isomer to the value of D_6 would be 0.128, *i. e.*, at least 0.608 molar in terms of concentration. Thus a minimum increase in *trans* isomer concentration of 0.0062 mole per liter was realized in this step. Assuming that the increase in *trans* concentration came through isomerization of the *cis* isomer, the concentration of *cis* at equilibrium was at least 0.0062 molar. This represents 9% conversion of the original *trans*-benzalacetone. The exposed solution after removal of excess *trans*-benzalacetone was treated with hydrochloric acid as before and there was observed an increase from $D_3 = 0.045$ to $D_7 = 0.059$. Once again if the maximum contribution of the *cis* isomer and other products is assumed to be 0.014, the contribution of *trans*-benzalacetone to this value is 0.045 (or 0.0213 mole per liter), an increase of 0.065 mole per liter (9% of the original concentration).

Chilling this latter solution (acid treated) to −24° yielded solid *trans*-benzalacetone (identified) while a blank of the previously chilled exposed solution showed no precipitate of any kind. The optical density (D_8) of the solution after acid treatment and chilling, and after proper dilution, was 0.040. Subtracting the solubility value (0.031) we find that the maximum contribution of the secondary products is 0.009.

Using this value for the maximum contribution of the secondary products to D_5, we get the value 0.133 (D_6 minus 0.009) for the actual contribution of the *trans* isomer. This corresponds to 0.0631 mole per liter or an increase over the original 0.0546 mole per liter of 0.0085 mole per liter. This is 12% of the original concentration of *trans*.

Some indication of the nature of the *cis*-benzalacetone curve was obtained by taking the absorption spectrum of the most favorable solution, from 220 to 350 mμ. There was observed only one peak (D_3) at 278.0 mμ. Subtracting the contribution of the *trans* compound present (0.031) from D_3 to give D_4 and subtracting the calculated contributions of the secondary products (0.009) the optical density for the *cis* isomer would be 0.005. Using the calculated concentration of the *cis* isomer at equilibrium (0.0085 molar) (8.5 × 10^{-7} molar at the standard dilution) the molar extinction coefficient for the *cis* isomer is 6 × 10^3. If conversion without secondary transformations were assumed the *cis* concentration would have been 0.0166 mole per liter at equilibrium, and using D_4 as the optical density the molar extinction coefficient would be 8 × 10^3.

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[4] *Cf.* Braude, *et al.*, *J. Chem. Soc.*, 1898 (1949).

N,N'-Dialkylmonoketopiperazines

BY WILLIAM B. MARTIN, JR.,[1] AND ARTHUR E. MARTELL

In this paper is described the conversion of a number of N,N'-dialkylethylenediamines prepared by Frost, *et al.*,[2] to the corresponding N,N'-dialkylmonoketopiperazines. Compounds of this type have not been reported previously. However, 2-ketopiperazine and its N-ethyl and N,N-dimethyl derivative have been prepared by Aspinall[3] while several N,N'-diaryl derivatives have been reported by Bischoff, *et al.*[4,5]

The preparative method consisted of heating the dialkyldiamine with slightly less than an equimolar amount of ethyl chloroacetate, which had been added very slowly to the reaction mixture. This procedure differed from that of Bischoff mainly in that no sodium acetate was used. The hydrochlorides of N,N'-disubstituted monoketopiperazines were extracted with benzene and purified by recrystallization from aqueous alcohol. The free bases were liberated by adding sodium hydroxide to the warm water–ethanol solution.

TABLE I

PREPARATION OF N,N'-DIALKYLMONOKETOPIPERAZINES

Alkyl	Reaction conditions Hours, total	Reaction conditions Temp., °C.	% Diamine recov.	% yield	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
Butyl	17	165	..	44	B. p. 132–134 (4 mm.)	13.19	12.84[a]
Octyl	5	145	..	6	1.5	7.76	7.78[b]
Dodecyl	10.5	165	..	10	36.5–37	6.42	6.19
Benzyl	5	135	38	10	83–84	9.99	10.13
Cyclohexyl	9	145	43	15	91–92	9.31	9.15[b]

[a] Calcd. for $C_{12}H_{24}N_2O$: C, 67.88; H, 11.39. Found: C, 67.55; H, 11.20. [b] Analyzed as the monohydrochloride.

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[1] Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

[2] Frost, Chaberek and Martell, THIS JOURNAL, **71**, 3842 (1949).

[3] Aspinall, *ibid.*, **62**, 1202 (1940).

[4] Bischoff and Nastvogel, *Ber.*, **22**, 1783 (1899); **23**, 2026, 2031, 2035 (1890).

[5] Bischoff and Trapesonzjanz, *ibid.*, **25**, 2931 (1892).