

tion coefficient is $6-8 \times 10^3$ 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 $m\mu$) in 100.0 ml. of iso-octane (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 $m\mu$ 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 $m\mu$ 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 $m\mu$.

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_8 , we get the value 0.133 (D_8 minus 0.009) for the actual contribution of the *trans* isomer.

(4) Cf. Braude, *et al.*, *J. Chem. Soc.*, 1893 (1949).

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 $m\mu$. There was observed only one peak (D_3) at 278.0 $m\mu$. 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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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 Aspinall³ 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		% Di-amine recov.	% yield	M. p., °C.	Nitrogen, %	
	Hours, total	Temp., °C.				Calcd.	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.

(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 Trapezonjanz, *ibid.*, **25**, 2931 (1892).

The dodecyl, benzyl and cyclohexyl derivatives thus obtained were purified by crystallization from water. The details of the preparation and properties of the products are given in Table I. The yields reported are quite low but since they represent the result of a first synthesis on a small amount of material, considerable improvement would be expected by further refinement of reaction conditions and method of isolation of the product. In this connection it is interesting to note that the correlation of % yield with reaction time and temperature indicate that considerable increase in yield should be possible in most cases by increasing both the temperature and time of reaction.

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Preparation of α -Naphthaleneacetic Acid by the Condensation of Naphthalene with Chloroacetic Acid

BY YOSHIRO OGATA AND JIRO ISHIGURO

The plant growth hormone α -naphthaleneacetic acid is ordinarily prepared by way of α -chloromethylnaphthalene and α -naphthaleneacetoneitrile.¹ Other procedures, in our hands at least, were less satisfactory.^{2,3} The direct condensation of naphthalene with chloroacetic acid⁴ has been reported to yield naphthaleneacetic acid, and we have investigated this reaction in detail. After preliminary experiments gave poor and non-reproducible yields, we studied the effect of many metals, metallic oxides and metal halides on this condensation and discovered that a small quantity of ferric salt was an excellent catalyst. It is probable that the small amount of iron (0.05–0.0008%) in coal tar naphthalene serves to promote the condensation in the examples previously described.⁴ Metallic bromides also promote the condensation, possibly by converting chloroacetic acid into bromoacetic acid, which condenses more easily,⁵ by way of hydrobromic acid.

Experimental

Materials.—Naphthalene purified by distillation, m. p. 80–80.5°, was used. Its iron content was determined by refluxing it with 2 *N* hydrochloric acid for one hour, oxidizing ferrous to ferric iron in the filtrate by means of chlorine and completing the determination colorimetrically with ammonium thiocyanate. The chloroacetic acid used melted at 61–63°. The bromoacetic acid, prepared by the bromination of acetic acid, had a boiling point of 112–117° (35 mm.).

Procedure.—Naphthalene (57.6 g.) (0.0010% iron), 14.1 g. of chloroacetic acid, 87.6 mg. of ferric oxide, and

(1) E. g., Cambron, *Can. J. Research*, **17B**, 10 (1939); *cf. C. A.*, **33**, 5387 (1939); Grummitt and Buck, "Organic Syntheses," Vol. XXIV, 1944, p. 30, and the literatures cited here.

(2) Criechl, *Chem. Ber.*, **80**, 410 (1947); *cf. C. A.*, **43**, 7749 (1948).

(3) Witman, U. S. Patent 2,290,401; *cf. C. A.*, **37**, 388 (1943).

(4) Wolfram, Schöring, Hausdörfer and I. G. Farbenind. A.-G., German Patent 562,391, Feb. 2, 1929; *cf. Frdl.*, **19**, 779 (1934).

(5) Demole, *Ber.*, **9**, 561 (1876).

420 mg. of potassium bromide were placed in a long-necked round-bottom flask fitted with a rubber stopper carrying a thermometer and an air-cooled tube about 1 m. long, and the mixture was boiled gently on a sand-bath for twenty hours. The best yield was obtained when the heating was controlled according to a temperature-time curve in which the temperature of reactants attained 200° after ten hours and 218° after twenty hours. After the reaction, the greater part of the unreacted naphthalene (43 g.) was recovered by distillation.⁶ The residue was extracted with hot sodium hydroxide solution, cooled and filtered. Acidification of the filtrate with hydrochloric acid yielded a brownish precipitate, 19.4 g. (70%), m. p. 108–113°. Crystallization from the 250-fold amount of boiling water with the addition of small amounts of concentrated hydrochloric acid gave 9.5 g. (34% based on chloroacetic acid, 45% on naphthalene reacted), m. p. 124–126°. The melting point could be raised to 132° by repeated crystallization and showed no depression when mixed with α -naphthaleneacetic acid prepared by the chloromethylation procedure. In the absence of ferric oxide and potassium bromide no naphthaleneacetic acid was produced. With potassium bromide alone 4% and with ferric oxide alone 5% was produced. The conditions described above are optimum with regard to temperature, time, increased amounts of potassium bromide and increased ratio of chloroacetic acid to naphthalene. Bromoacetic acid condensation is more rapid, but the high cost and skin irritant properties of this substance render it less suitable than chloroacetic acid. The promoting action of several other metallic halides (e. g., sodium chloride, potassium chloride, potassium iodide, hydrated aluminum chloride, hydrated aluminum bromide, hydrated ferric bromide and mercuric bromide), when mixed with ferric oxide, was also observed, but these were less effective than potassium bromide.

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(6) The chloroacetic acid reacted almost completely, and could not be recovered.

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Decomposition of the Isomeric Valeric Acids in the Ozonizer Discharge

BY WILLIAM S. PARTRIDGE¹ AND WARREN M. GARRISON

In the alpha particle bombardment of a series of straight chain aliphatic acids,² it has been observed³ that the abundance of hydrogen relative to carbon dioxide plus carbon monoxide in the product gas is proportional to the ratio of C–H to C–COOH bonds in the bombarded molecule. Data reported⁴ earlier for cathode ray bombardment of aliphatic hydrocarbons show a similar group to product relationship for hydrogen and methane. If the H₂/CH₄ yield ratios for the series of hydrocarbons studied are plotted *versus* the C–H/C–CH₃ bond ratios, a straight line relation-

(1) Department of Chemistry, University of Utah.

(2) C. W. Sheppard and V. L. Burton, *THIS JOURNAL*, **68**, 1636 (1946).

(3) R. E. Honig, *Science*, **104**, 27 (1946).

(4) C. S. Schoepfle and C. H. Fellows, *J. Ind. Eng. Chem.*, **23**, 1396 (1931).