reflux for 15 hr.[9] The solution was concentrated under reduced pressure to give a residue (freely soluble in absolute ethanol) which was recrystallized from ethyl acetate to afford 105 mg. (74%); m.p. 145–155°.

Ethyl 1-methyl-5-oxo-3-pyrrolidinecarboxylate was prepared by vacuum distillation (after filtration of methylamine hydrobromide) of the product from treatment of diethyl bromomethylsuccinate[10] with 3 equivalents of 3.5 *N* ethanolic methylamine at 0°; b.p. 167–168°/20.5 mm.[11]; d_{20}^{20} 1.1170; $n^{25}D$ 1.4620; M_D calcd.: 42.43; M_D found: 42.13.

Anal. Calcd. for $C_8H_{13}NO_3$ (171.18): C, 56.12; H, 7.65. Found: C, 56.10; H, 7.55.

1-Methyl-5-oxo-3-pyrrolidinecarboxamide (VI).—To 5 ml. of concentrated aqueous ammonia at 0° was added 113 mg. (0.0005 mole) of dimethyl methylaminomethylsuccinate hydrochloride (III). After 20 hr. at 0°, the solution was concentrated under diminished pressure to give a residue which was triturated with chloroform to discard 22 mg. of insoluble ammonium chloride. The chloroform filtrate was concentrated under reduced pressure to give a residue which was recrystallized from a mixture of methanol and ethyl acetate to afford 60 mg. (85%) of plates; m.p. 140–142°[12]; infrared spectrum: 5.95, 6.05, 6.15, 6.65 μ (amide bands).

Anal. Calcd. for $C_6H_{10}N_2O_2$ (142.16): C, 50.69; H, 7.09; N, 19.71. Found: C, 50.97; H, 7.21; N, 19.88.

Methyliminodi(methylsuccinic) Acid (IV).—To a solution of 483 mg. (0.003 mole) of methylaminomethylsuccinic acid (II) and 486 mg. (0.003 mole) of carboxysuccinic acid (I) in 1 ml. of water was added 0.25 ml. of 37% aqueous formaldehyde (equivalent to 100 mg. or 0.0033 mole of formaldehyde); a brisk evolution of carbon dioxide commenced within a few minutes. A precipitate, which began to form within 1 hr., had completely pervaded the solution after 2 hr. The mixture was kept at 25° for 2 days, diluted with 2 ml. of water, and heated to dissolve the product. After 20 hr. at 25°, followed by 2 days at 0°, the precipitate was collected by filtration and recrystallized from water to afford 255 mg. (29%) of plates; m.p. 180–183°; infrared spectrum: 5.80, 5.85 μ (carboxyl).

Anal. Calcd. for $C_{11}H_{17}NO_8$ (291.26): C, 45.36; H, 5.89; N, 4.81. Found: C, 45.33; H, 5.92; N, 4.85.

Tetramethyl Methyliminodi(methylsuccinate) Hydrochloride.—To 2.5 ml. of methanol at 0° was added dropwise, with cooling, 357 mg. (0.22 ml.) (0.003 mole) of thionyl chloride; after 1 hr. at 0°, 146 mg. (0.0005 mole) of methyliminodi(methylsuccinic) acid (IV) was added. After 2 days at 0°, followed by 2 days at 25°, the solution was concentrated under diminished pressure to give a remainder from which 20 ml. of toluene was vacuum distilled. Two recrystallizations of the residue from ethyl acetate gave 165 mg. (86%) of needles; m.p. 117–121°; infrared spectrum: 4.20, 4.30 (substituted ammonium), 5.80 μ (ester).

Anal. Calcd. for $C_{15}H_{26}NO_8Cl$ (383.83): C, 46.93; H, 6.83; N, 3.65. Found: C, 47.15; H, 6.80; N, 3.57.

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(9) Cyclization proceeded to a lesser extent during short periods of reflux as shown by incomplete solubility of the reaction residue in absolute ethanol; *cf.* the conversion of aqueous glutamic acid to 5-oxo-2-pyrrolidinecarboxylic acid: J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," Vol. 3, J. Wiley & Sons, Inc., New York, N. Y., 1961, pp. 1934–1937.

(10) R. Anschütz and F. Reuter, *Ann.*, **254**, 144 (1889). In the older literature, bromomethylsuccinic acid was known as "itabrompyrotartaric acid."

(11) *Cf.* the preparation from diethyl itaconate with methylamine: Y. H. Wu and R. F. Feldkamp, *J. Org. Chem.*, **26**, 1519 (1961).

(12) *Cf.* the preparation from dimethyl itaconate with one equivalent of methanolic methylamine followed by excess methanolic ammonia: H. C. Scarborough, J. L. Minielli, B. C. Lawes, W. G. Lobeck, Jr., J. R. Corrigan, and Y. H. Wu, *ibid.*, **26**, 4955 (1961).

Acyl Derivatives of 3,4-Dihydro-4-oxobenzo-1,2,3-triazine

M. S. GIBSON AND A. W. MURRAY

Chemistry Department, Faculty of Technology, The University, Manchester 1, England

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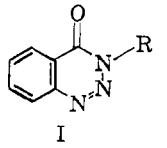
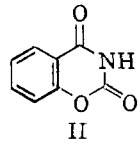
Heller[1] has reported the preparation of an acetyl and a benzoyl derivative of 3,4-dihydro-4-oxobenzo-1,2,3-triazine (I, R = H) by reaction of the sodium or silver salt with the appropriate acid chloride. These compounds were formulated as lactam (*i.e.* *N*-acyl) derivatives rather than lactim (*O*-acyl) derivatives since (i) methylation under similar conditions had been shown to give the *N*-methyl derivative (I, R=Me), and (ii) ethoxycarbonylation had given an ethoxycarbonyl derivative which was degraded by hot hydrochloric acid to (II); the latter compound contains nitrogen linked to two carbonyl groups, thus implying formula (I, R = COOEt) for the ethoxycarbonyl derivative, assuming that no lactim–lactam isomerisation occurs under the influence of acid.



I



II

In two recent reviews of triazine chemistry,[2,3] the possibility that these compounds are *O*-acyl derivatives has been revived, and, without further evidence, the lactim formulation has actually been adopted for purposes of tabulation.

However, the infrared spectra of both the acetyl and the benzoyl derivative show two absorption bands due to carbonyl in the 1750–1650-cm.$^{-1}$ region. In this respect, these compounds resemble the *N*-acylisocarbostyrils, but differ from, *e.g.*, 2-benzoyloxypyridine and 4-acetoxyisoquinoline which show only one such band (at 1740 cm.$^{-1}$).[4] The ultraviolet absorption spectrum of the acetyl derivative is similar to that of the parent compound, though shifted to shorter wave length;

(1) G. Heller, *J. prakt. Chem.*, (2) **111**, 1 (1925).

(2) J. G. Erickson, "The Chemistry of Heterocyclic Compounds," Vol. 10, A. Weissberger, ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 17.

(3) J. P. Horwitz, "Heterocyclic Compounds," Vol. 7, R. C. Elderfield, ed., J. Wiley & Sons, Inc., New York, N. Y., 1961, p. 787.

(4) M. M. Robison and B. L. Robison, *J. Org. Chem.*, **21**, 1337 (1956).

that of the benzoyl derivative shows the same shift, masked partly, however, by additional absorption due to the benzoyl group.

We conclude, therefore, that, as in the case of isocarbostyril,[4] acylation of 3,4-dihydro-4-oxobenzo-1,2,3-triazine (I, R = H) yields the *N*-acyl derivatives (I, R = COMe, COPh), as originally suggested by Heller.

Experimental

Ultraviolet absorption spectra were determined for ethanol solutions (Higler Unicam spectrophotometer); infrared spectra were measured for Nujol and hexachlorobutadiene mulls (Perkin-Elmer 21 spectrophotometer). Compounds were prepared by Heller's methods; experimental details are given below in cases where his information is incomplete.

3,4-Dihydro-4-oxobenzo-1,2,3-triazine occurred as needles (from ethanol), m.p. 210° dec. (Heller, m.p. 213° dec.), ν_{max} 3140 (N—H) and 1695 cm.$^{-1}$ (C:O), λ_{max} 209 (ϵ 17,100), 225 (ϵ 20,050) and 281 mμ(ϵ 6100), λ_{min} 212 (ϵ 16,670) and 257 mμ (ϵ 3600), λ_{infl} 294 (ϵ 4300) and 305 mμ (ϵ 2750).

3-Acetyl-3,4-dihydro-4-oxobenzo-1,2,3-triazine.—Silver acetate (1.2 g.), dissolved in aqueous ethanol, was added with shaking to the triazine (1.1 g.) in warm ethanol. The silver salt separated as a white solid, was collected, and dried *in vacuo*.

Freshly distilled acetyl chloride (1 ml.) was added to a suspension of the silver salt (1.5 g.) in dry benzene (30 ml.), and the mixture was refluxed for 30 min. After standing overnight at room temperature, the silver chloride was removed, and the filtrate evaporated. The residual orange sirup slowly solidified. The acetyl derivative (0.7 g.) was crystallized from water, dried, and recrystallized from light petroleum (b.p. 100–120°), forming needles, m.p. 165° (Heller, m.p. 165°), ν_{max} 1695 and 1655 cm.$^{-1}$ (C:O) [*cf.* *N*-acetylisocarbostyril,[4] ν_{max} 1705 and 1665 cm.$^{-1}$], λ_{max} 219 (ϵ 23,100), 252 (ϵ 11,360) and 298 mμ (ϵ 4320), λ_{min} 239 (ϵ 9900) and 272 mμ (ϵ 3580), and λ_{infl} 261 mμ (ϵ 8400).

3-Benzoyl-3,4-dihydro-4-oxobenzo-1,2,3-triazine.—The triazine (1.5 g.) in warm ethanol was treated with sodium ethoxide (from 0.24 g. of sodium) in ethanol (30 ml.). After standing overnight at room temperature, ethanol was removed *in vacuo;* trituration of the residue with dry toluene gave the sodium salt (1.8 g.) as a white solid. This was converted to the benzoyl derivative (1 g.), which separated from light petroleum (b.p. 100–120°) as needles, m.p. 132° (Heller, m.p. 132–133°), ν_{max} 1718 and 1690 cm.$^{-1}$ (C:O), λ_{max} 209 (ϵ 26,150) and 227 mμ (ϵ 28,800), λ_{min} 213 mμ (ϵ 24,900), λ_{infl} 249 (ϵ 14,800) and 276 mμ (ϵ 9850).

Equilibration of *cis*- and *trans*-α-Methylstilbene in Presence of Potassium *t*-Butoxide as Catalyst[1]

ANDRZEJ ZWIERZAK[2] AND HERMAN PINES

The Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois

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Incidental to the study of base-catalyzed reactions of alkenyl-benzenes *cis*- and *trans*-α-methylstilbenes have been equilibrated in the presence of catalytic amounts of potassium *t*-butoxide at 139 ± 1° and 200 ± 1°. The equilibrium mixture consisted, respectively, of 21.0% and 21.2% *cis*-, 76.8 and 74.0% *trans*-α-methylstilbene, and 2.2 and 4.8% 2,3-diphenyl-1-propene.

Cis- and *trans*-α-methylstilbene were synthesized by a modification of the procedure described by Abd Elhafez and Cram[3]. A mixture of the two diastereomers of 1,2-diphenyl-1-propanol was transformed to a solid mixture of two diastereomeric chlorides by the action of thionyl chloride in the presence of pyridine. The chlorides were separated into distinct diastereomeric species by fractional crystallization and subsequently dehydrohalogenated by means of 5% ethanolic potassium hydroxide[4] to give pure *cis*- and *trans*-α-methylstilbenes. Attempted preparation of pure *cis*-α-methylstilbene by the method described by Simamura and Suzuki[5] failed although the *trans* isomer was obtained in pure form. The equilibration reactions were made by refluxing a solution of methylstilbenes in either xylene or decahydronaphtalene in the presence of 0.1 *M* equivalent of potassium *t*-butoxide, based on the stilbenes used.

Starting with *trans* isomer in xylene solution (temp. 139 ± 1°), the equilibrium was reached after twenty-four hours while at 200°, in decahydronaphtalene solution, within one hour equilibrium was achieved. The progress of the reaction was investigated by taking out samples during the reaction and analyzing by gas chromatography. Equilibration reactions were also made using either pure *cis*-α-methylstilbene or a mixture of methylstilbenes enriched in the *cis* isomer.

It was found that 2,3-diphenyl-1-propene was formed in equilibrium concentration shortly after the reflux temperature of the solvent was reached; the double bond migration was much faster than the *cis-trans* isomerization. The composition of 1,2-diphenylpropenes at equilibrium is summarized in Table I. The hydrogenation of the equilibrated mixture produced only 1,2-diphenylpropane, which shows that the compounds present had the same skeleton as the starting α-methylstilbene.

TABLE I

EQUILIBRIUM MIXTURE OF *cis*- AND *trans*-α-METHYLSTILBENE AND 2,3-DIPHENYL-1-PROPENE

Temperature (±1°)	139°	200°
cis-α-Methylstilbene, %	21.0	21.2
trans-α-Methylstilbene, %	76.6	74.0
2,3-Diphenyl-1-propene, %	2.4	4.8

(1) Paper XXIV of the series Base Catalyzed Reaction. For paper XXIII, see J. Shabtai, E. M. Lewicki, and H. Pines, *J. Org. Chem.*, **27**, 2618 (1962).

(2) On leave of absence from Polytechnic Institute, Lodz, Poland.

(3) F. A. Abd Elhafez and D. J. Cram, *J. Am. Chem. Soc.*, **75**, 340 (1953).

(4) E. Ellingboe and R. C. Fuson, *ibid.*, **55**, 2960 (1933).

(5) O. Simamura and H. Suzuki, *Bull. Chem. Soc. Japan*, **27**, 234 (1954).