termined in aqueous solution with a Cary Model 14 spectrophotometer; the infrared spectra were determined in pressed potassium bromide disks with a Perkin-Elmer Model 221 spectrophotometer; the proton magnetic resonance spectrum was determined as a 10% (w./v.) solution in dimethyl sulfoxide-d_6 with a Varian Associates Model A-60 spectrometer.

9-Allyladenine (IIa).—A suspension of 1.35 g. (10.0 mmoles) of adenine (Ia) and 1.52 g. (10.1 mmoles) of anhydrous potassium carbonate in 100 ml. of N,N-dimethylacetamide containing 0.88 ml. (10.0 mmoles) of allyl bromide was stirred at 130° for 18 hr. After filtration the solution was evaporated to dryness *in vacuo*. The residue was dissolved in 100 ml. of chloroform. The chloroform solution was washed with 25 ml. of water, dried over magnesium sulfate, and evaporated to dryness *in vacuo*. The residue crystallized from ethanol–acetonitrile: yield, 471 mg. (27%); m.p. 143–145°; λ_{max} in mμ ($\epsilon \times 10^{-3}$), at pH 1 260 (13.7), pH 7 261 (13.8), and pH 13 261 (13.8); $\bar{\nu}$ in cm.$^{-1}$, 3300 (NH), 3150 and 3100 (CH), 1650 (NH), and 1595 and 1570 (C=C, C=N).

This material was identical with an authentic sample of 9-allyladenine prepared in another manner.[13]

Examination of the filtrate showed that it contained about an equal mixture of 3- and 9-allyladenine.

9-Propenyladenine (IIIa).—To a solution of 184 mg. (1.00 mmole) of potassium *t*-butoxide in 3.7 ml. of dimethyl sulfoxide was added 175 mg. (1.00 mmole) of 9-allyladenine. The resulting solution was heated in a 100° oil bath for 20 min., diluted with 3.7 ml. of water, and taken to pH 8 with solid carbon dioxide. The thick sludge that resulted was evaporated to dryness *in vacuo*. A suspension of the residue in 25 ml. of water was extracted with three 50-ml. portions of chloroform. After drying over magnesium sulfate, the chloroform solution was evaporated to dryness *in vacuo*. A white solid residue remained: yield, 144 mg. (82%); m.p. 197°; λ_{max} in mμ ($\epsilon \times 10^{-3}$), at pH 1 233 (20.8) and 256 (sh) (14.4), pH 7 260 (13.1), and pH 13 260 (12.7); $\bar{\nu}$ in cm.$^{-1}$, 3370 and 3310 (NH), 3140 (CH), 1645 (NH), 1590 and 1570 (C=C, C=N), and 1470 (C—CH$_3$); τ in p.p.m., 8.1 and 8.2 (C=H—CH$_3$). This material was used in the next step without further purification.

1-Methyl-9-propenyladenine (IVa).—To a solution of 381 mg. (2.18 mmoles) of 9-propenyladenine in 30 ml. of N,N-dimethylformamide was added slowly 0.31 ml. (5.00 mmoles) of methyl iodide. The solution was sealed tightly and stirred at room temperature for 18 hr. It was then evaporated to dryness *in vacuo*. A solution of the residue in 100 ml. of water was brought to pH 10 with concentrated ammonium hydroxide. Evaporation of the solution to 20 ml. gave a white precipitate: yield, 396 mg. (57%); m.p. 298–300°; λ_{max} in mμ ($\epsilon \times 10^{-3}$), at pH 1 231 (20.6) and 256 (sh) (9.15), pH 7 227 (20.0) and 256 (sh) (8.84), and pH 13 226 (18.3) and 256 (sh) (8.30); $\bar{\nu}$ in cm.$^{-1}$, 3310 (NH), 3160 and 3040 (CH), 1690 and 1630 (NH and C=C), 1595, 1575, and 1510 (C=C, C=N), and 1470 (C—CH$_3$). The analytical sample was obtained by recrystallization from ethanol.

Anal. Calcd. for $C_9H_{11}N_5 \cdot HI$: C, 34.07; H, 3.81; N, 22.08. Found: C, 34.28; H, 4.08; N, 22.08.

1-Methyladenine (VIa).—A solution of 200 mg. (0.628 mmole) of 1-methyl-9-propenyladenine hydroiodide in 15 ml. of 0.5 *N* methanolic sodium hydroxide was treated with a 4% aqueous potassium permanganate solution. After the dark brown precipitate that formed became very thick, it was removed by filtration and the addition of permanganate resumed. This process was continued until a brown color no longer developed, and an aliquot of the reaction mixture showed no starting compound when examined by thin layer chromatography. Evaporation of the methanol in a nitrogen stream left an aqueous solution that produced a crystalline precipitate: yield, 60 mg. (64%); m.p. 310–312° dec.; λ_{max} in mμ ($\epsilon \times 10^{-3}$), at pH 1 257 (11.7), pH 7 264 (10.8), and pH 13 269 (14.1); $\bar{\nu}$ in cm.$^{-1}$, 3400 (NH), 3240 and 2950 (CH), 2900–2600 (acidic NH), and 1690, 1645, and 1555 (NH, C=C, C=N). The ultraviolet spectra agree with the literature values.[14] A thin layer chromatogram run on 60 μl. of this material on silica gel H using 1:1 chloroform–methanol as solvent showed only one ultraviolet absorbing spot when sprayed with Ultraphor. N^6-Methyladenine, run as a standard on the same plate, traveled much further than 1-methyladenine.

9-Propenylhypoxanthine (IIIb).—To a solution of 552 mg. (3.00 mmoles) of potassium *t*-butoxide in 11 ml. of dimethyl sulfoxide (dried with molecular sieve) was added 528 mg. (3.00 mmoles) of 9-allylhypoxanthine.[15] The resulting solution, protected by a calcium chloride tube, was heated in a 95° oil bath for 20 min., then cooled to room temperature, diluted with 30 ml. of water, and taken to pH 7 with solid carbon dioxide. After the mixture was cooled, the precipitate that had formed was collected by filtration: yield, 440 mg. (83%); m.p. 301–303° dec.; λ_{max} in mμ ($\epsilon \times 10^{-3}$), at pH 1 227 (16.8) and 248 (sh) (10.5), pH 7 226 (21.8) and 250 (sh) (10.8), and pH 13 220 (20.7), 254 (9.90), and 267 (sh) (6.98); $\bar{\nu}$ in cm.$^{-1}$, 3045 and 2850 (CH), 2800–2600 (acidic H), 1685 (C=O), 1585, 1570, and 1510 (C=C, C=N), and 1470 (C—CH$_3$). This material was used in the next step without further purification.

1-Methyl-9-propenylhypoxanthine (IVb).—A solution of 352 mg. (2.00 mmoles) of 9-propenylhypoxanthine and 372 mg. (2.00 mmoles) of methyl *p*-toluenesulfonate in 30 ml. of N,N-dimethylacetamide containing a suspension of 324 mg. (2.35 mmoles) of anhydrous potassium carbonate was stirred and heated at 100° for 2 hr. The inorganics were removed by filtration and the solution evaporated to dryness *in vacuo*. The residue was partitioned between chloroform and water. The chloroform layer, after drying over magnesium sulfate, was evaporated to dryness *in vacuo*. A white crystalline residue was obtained: yield, 357 mg. (94%); m.p. 220°; λ_{max} in mμ ($\epsilon \times 10^{-3}$), at pH 1 220 and 253 (sh) (9.06), pH 7 225, 254 (sh) (8.38), and 270 (sh) (5.00), and pH 13 225, 254 (sh) (8.74), and 270 (sh) (5.15); $\bar{\nu}$ in cm.$^{-1}$, 3090, 3040, 2960, 2920, 2860 (CH), 1665 (C=O), 1570, 1535 and 1510 (C=C, C=N), and 1450 (C—CH$_3$). The analytical sample was obtained by recrystallization from ethanol: m.p. 220°.

Anal. Calcd. for $C_9H_{10}N_4O$: C, 56.84; H, 5.30; N, 29.44. Found: C, 57.08; H, 5.50; N, 29.50.

1-Methylhypoxanthine (VIb).—To a solution of 357 mg. (1.88 mmoles) of 1-methyl-9-propenylhypoxanthine in 15 ml. of 0.5 *N* methanolic sodium hydroxide there was added dropwise a 4% aqueous potassium permanganate solution. After the dark brown precipitate that formed became very thick, it was removed by filtration and the addition of permanganate resumed; the process was repeated. The addition of permanganate was continued until there was no longer a brown color. The colorless reaction solution was taken to pH 5 with dilute hydrochloric acid and evaporated to dryness *in vacuo*. The residue crystallized from water: yield, 164 mg. (58%); m.p. above 260°; λ_{max} in mμ ($\epsilon \times 10^{-3}$), at pH 1 249 (9.40), pH 7 250 (9.00), and pH 13 260 (9.60); $\bar{\nu}$ in cm.$^{-1}$, 3080, 3040, 2920, 2860 (CH), 2800–2500 (acidic NH), 1690 (C=O), and 1585 and 1530 (C=C, C=N). The ultraviolet spectra agree with the literature values[17] and with those of a sample of 1-methylhypoxanthine prepared by the method of Shaw.

---

[15] This compound was prepared from 5-amino-4,6-dichloropyrimidine[18] by the procedure developed in these laboratories.[16]

[16] C. Temple, Jr., C. L. Kussner, and J. A. Montgomery, *J. Med. Pharm. Chem.*, **5**, 866 (1962).

[17] L. Townsend and R. K. Robins, *J. Org. Chem.*, **27**, 991 (1962).

The Monomolecular and Bimolecular Reduction of Aryl Olefins

DONALD R. WEYENBERG

Organic Research Laboratory of the Dow Corning Corporation, Midland, Michigan 48641

Received May 17, 1965

Recent studies have confirmed the similarity of the mechanisms of the disilylation reaction[1-4] and of the

---

[1] D. R. Weyenberg and L. H. Toporcer, *J. Am. Chem. Soc.*, **84**, 2843 (1962).

[2] D. R. Weyenberg and L. H. Toporcer, *J. Org. Chem.*, **30**, 943 (1965).

[3] D. R. Weyenberg, L. H. Toporcer, and A. E. Bey, *J. Am. Chem. Soc.*, in press.

[4] D. R. Weyenberg, L. H. Toporcer, and M. J. Napoli, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961, p. 31Q.

chemical reduction[5] of carbon–carbon unsaturated compounds. Both reactions involve the trapping of organometallic reagents formed from an alkali metal and an unsaturated organic compound. A protic solvent serves as trapping agent in the chemical reduction, and a chlorosilane is the trapping agent in the disilylation reaction. The unusual phenomenon noted in the latter synthesis,[3] whereby the disilylation of aryl olefins with lithium in tetrahydrofuran (THF) could be directed toward monomolecular or bimolecular products by minor changes in trapping agent to olefin ratio, prompted a short reinvestigation of the chemical reduction of an aryl olefin at various ratios of proton source to olefin. We now wish to report that the same phenomenon is noted in the chemical reduction of α-methylstyrene and to suggest a convenient method for directing the chemical reduction of aryl olefins to monomolecular or bimolecular products.

The chemical reduction of monoaryl olefins has usually given the monomolecular product. Thus, styrene yields ethylbenzene with lithium and ethylaniline,[6] sodium in ammonia,[7] or $Ca(NH_3)_6$ in ether[8] and yields 1-ethylcyclohexene with lithium in methylamine.[9] In these typical reduction procedures a large excess of the proton source is employed. A bimolecular reduction of α-methylstyrene to 2,5-diphenylhexane was accomplished by Frank, *et al.*,[10] *via* a two-step procedure.

$$PhMeC{=}CH_2 + Na \xrightarrow[THF]{-70^\circ} \underset{A}{NaCPhMe(CH_2)_2CPhMeNa}$$

$$A + H_2O \longrightarrow (PhMeCHCH_2)_2$$

In the current study the reduction of α-methylstyrene in tetrahydrofuran with lithium and varying amounts of ethanol was investigated. Changing the ratio of olefin to alcohol from the stoichiometry required for monomolecular reduction to that required for bimolecular reduction had a dramatic effect on the course of the reduction. Whereas a 2:1 ratio of alcohol to olefin gave mainly monomolecular reduction, an equal molar ratio of alcohol and olefin gave mainly bimolecular reduction. The structural assignment for

$$PhMeC{=}CH_2 + 2EtOH + 2Li \xrightarrow{THF} PhCMe_2H$$

$$2PhMeC{=}CH_2 + 2EtOH + 2Li \xrightarrow{THF} \underset{65\%}{(PhMeCHCH_2)_2}$$

the 2,5-diphenylhexane from the latter reaction was confirmed by its relatively simple H^1 n.m.r. pattern. The *d,l* and *meso* isomers of this compound were separated by fractional crystallization.

This tendency for the reagents to combine in the ratio present in the solution was also noted in the disilylation of styrene and α-methylstyrene under the above conditions and again confirms the similarity between these two synthetic procedures. The reasons for this interesting phenomenon have been discussed.[3]

Experimental

Bimolecular Reduction.—The addition of a mixture of 18.4 g. (0.4 mole) of ethanol and 47.2 g. (0.4 mole) of α-methylstyrene to 5.6 g. (0.8 g.-atom) of lithium in 200 ml. of THF during 10 min. gave an extremely exothermic reaction. The temperature was maintained at 20–40° by external cooling. Distillation after filtration and extraction with dilute hydrochloric acid gave less than 1 g. of cumene, 30.9 g. (65%) of 2,5-diphenylhexane (b.p. 140° at 1.5 mm.; n^{25}_D 1.5392), and 8.85 g. (19%) of residue.

Anal. Calcd. for $C_{18}H_{22}$: C, 90.7; H, 9.3. Found: C, 90.9, 91.2; H, 9.52, 9.51.

Fractional crystallization from MeOH at 0° gave a crystalline isomer (m.p. 44.5–46.2° after two recrystallizations) and a liquid isomer (m.p. below 0°). The infrared solution spectra of the two isomers and the original mixture were identical from 2–15 μ. The H^1 n.m.r. spectra showed the CH_3 doublets at τ 8.86, multiplets for CH_2 at 8.55, multiplets for CH at 7.46, and $C_{ar}H$ at 2.95 in a ratio of 3:2:1:5. The spectra for the two isomers were identical except for different splitting patterns for CH_2.

Monomolecular Reduction.—The rapid addition of a mixture of 23.6 g. (0.2 mole) of α-methylstyrene and 18.4 g. (0.4 mole) of ethanol to 5.3 g. (0.76 g.-atom) of lithium in 200 ml. of THF gave a mildly exothermic reaction. The reduction, which was complete in 1.5 hr., gave a 4:1 ratio of cumene to 2,5-diphenylhexane by v.p.c. analysis.

---

(5) For an excellent review of chemical reduction see H. Smith, "Organic Reactions in Liquid Ammonia," Vol. I, Part 2, Interscience Publishers, Inc., New York, N. Y., 1963., pp. 151–280.

(6) K. Ziegler, L. Jakob, H. Wollthan, and A. Wenz, *Ann.*, **511**, 64 (1934); *Chem. Abstr.*, **28**, 5431 (1934).

(7) C. B. Wooster and J. F. Ryan, *J. Am. Chem. Soc.*, **56**, 1133 (1934).

(8) H. Boer and P. M. Duinker, *Rec. trav. chim.*, **77**, 346 (1958); *Chem. Abstr.*, **52**, 15485*g* (1958).

(9) R. A. Benkesser, C. Arnold, Jr., and R. F. Lambert, *J. Am. Chem. Soc.*, **77**, 6042 (1955).

(10) C. E. Frank, J. R. Leebrick, L. F. Moormeier, J. A. Scheben, and O. Homberg, *J. Org. Chem.*, **26**, 307 (1961).

Synthesis and Properties of Fluorine-Containing Heterocyclic Compounds. III. Substituted Tetrahydropyrans[1]

ADRIENNE STEINACKER DEY[2] AND MADELEINE M. JOULLIÉ

Department of Chemistry, University of Pennsylvania,
Philadelphia, Pennsylvania 19104

Received March 18, 1965

When ethyl trifluoroacetoacetate was treated with various aliphatic and aromatic aldehydes using the usual Knoevenagel conditions, the products obtained appeared to be monohydrates of the expected bisesters based on their elemental analysis. All the compounds obtained were white crystalline solids with fairly low melting points (95–125°), and no signs of decomposition were observed on melting. The one molecule of water which was included in the empirical formula of all the products could not be removed by prolonged drying at 0.1 mm. or by azeotropic distillation. When these compounds were treated with a ferric chloride solution or ceric nitrate reagent, they did not give a positive test as would be expected if they contained hydroxyl groups. The infrared spectra of these compounds did not show evidence for enolic double bonds. Attempts to prepare copper chelates also failed thus indicating the absence of β-keto structures. Oximes or 2,4-dinitrophenylhydrazones of some of the compounds could not be obtained under the normal conditions used to prepare these derivatives. This showed the absence of normal carbonyl groups. A molecular weight determination on the product formed from ethyl trifluoro-

---

(1) Preceding paper in this series: A. S. Dey and M. M. Joullié, *J. Heterocyclic Chem.*, in press.

(2) Abstracted from a portion of the Ph.D. thesis of A. S. Dey, University of Pennsylvania, 1964.