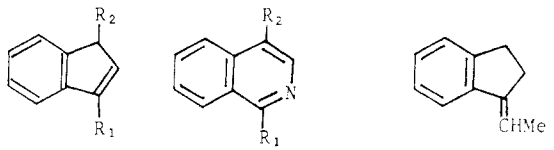
Table I. Conversion of Indenes to Isoquinolines

indene	isoquinoline	yield, %
1a	2a	73
1b	2b	57
1c	2c	56
1d + 3	2d	56[a] (80[b])
1e	2e	77

[a] Based on starting material (1d + 3). [b] Based on estimated amount of 1d in starting material.

version. Attempts to increase the rate of the process were not successful; the oxidation processes have a complex pH dependence, and ammonia deactivates osmium tetraoxide.[4]

We turned, therefore, to a two-step, "one-pot" procedure in which the oxidation step used 2 equiv of sodium metaperiodate and a catalytic amount of osmium tetraoxide in a 5:2 mixture of *tert*-butyl alcohol and a phosphate buffer of pH 8; the indene was normally oxidized within 5 h under these conditions. Ammonium acetate was then



1 2 3

a $R_1 = R_2 = H$

b $R_1 = Me$; $R_2 = H$

c $R_1 = Ph$; $R_2 = H$

d $R_1 = Et$; $R_2 = H$

e $R_1 = H$; $R_2 = Me$

added, and the isoquinoline produced could be isolated by standard procedures; isoquinoline itself was isolated in 73% yield by this method. Indenes carrying an alkyl or phenyl substituent on the olefinic double bond were also converted to isoquinolines in acceptable yields by this method. Under some of the reaction conditions we investigated initially, these compounds gave poor results, as might have been anticipated since it has been pointed out[5] that it is often difficult to dihydroxylate trisubstituted olefins under catalytic conditions.

One route to substituted indenes is by the dehydration of the Grignard product of the indanone, but this may produce a mixture of isomers; for example, when the ethyl Grignard reagent was used, a mixture of **1d** and **3** was obtained. As the fourth entry in Table I shows, it is unnecessary to separate the isomer with an exocyclic double bond before carrying out the conversion to the isoquinoline. Another route to substituted indenes is the alkylation of the indenyl anion, and the 1-alkylindene may be isolated from this reaction, but tautomerism to the 3-alkylindene can readily occur.[6] However, 1-methylindene (**1e**) was cleanly converted to 4-methylisoquinoline (**2e**) under the conditions described; no **2b** was detected in the product by ^1H NMR spectroscopy, showing that no appreciable tautomerism of **1e** had occurred during the reaction.

This procedure has proven to be a convenient method for the conversion of a range of simple indenes to isoquinolines, and its applicability to more complex examples will be investigated further.

Experimental Section

Isoquinoline Synthesis. A solution of indene (1.16 g, 10.0 mmol) in 50 mL of *tert*-butyl alcohol was prepared in a 250-mL flask equipped with a magnetic stirrer, and osmium tetraoxide (38 mg, 0.15 mmol) was added to the stirred solution. After 5 min, sodium metaperiodate (4.7 g, 22.0 mmol) and 30 mL of phosphate buffer (pH 8: 50 mL of 0.1 M KH_2PO_4 and 46.7 mL 0.1 M NaOH made up to 100 mL) were added. After 5 h (or when a flocculent, white precipitate appeared and the green color of the solution faded, signaling completion of the oxidation), ammonium acetate (7.7 g, 0.1 mol) was added, and stirring was continued for 30 min. The mixture was poured into 150 mL of dilute hydrochloric acid, and the resulting mixture was extracted with ether. The aqueous phase was made basic with concentrated aqueous ammonia and thoroughly extracted with ether. This ether extract afforded isoquinoline (0.95 g, 7.3 mmol) which was purified by vacuum distillation; picrate, mp 223–225 °C (lit.[7] mp 225–226 °C).

The same procedure with the same molar quantities of reactants was used in the preparation of substituted isoquinolines, and the results are listed in Table I. 3-Ethylindene was prepared from 1-indanone by Grignard reaction with ethylmagnesium bromide and dehydration of the alcohol produced with sulfuric acid in benzene. A 7:3 mixture of 3-ethylindene and 1-ethylideneindan (NMR integration) was obtained; this mixture of isomers (1.44 g, 10.0 mmol) was converted to 1-ethylisoquinoline (0.88g, 5.6 mmol). 1-Methylindene was prepared by treatment of indene sequentially with butyllithium and methyl sulfate.[6] The ^1H NMR spectra of all products were in accord with the structures assigned. Free bases were distilled under reduced pressure and converted to their crystalline picrates: 1-methylisoquinoline picrate, mp 226–227 °C (lit.[7] mp 225–226 °C); 1-phenylisoquinoline picrate, mp 165–166 °C (lit.[7] mp 165–166 °C); 1-ethylisoquinoline picrate, mp 208–210 °C (lit.[7] 209–210 °C); 4-methylisoquinoline picrate, mp 209–211 °C, with sublimation and remelting at 218 °C (lit.[8] mp 212–216 °C). Melting points were determined on a Thomas-Kofler micro hot stage.

Acknowledgment. This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

Registry No. **1a**, 95-13-6; **1b**, 767-60-2; **1c**, 1961-97-3; **1d**, 2294-91-9; **1e**, 767-59-9; **2a**, 119-65-3; **2a** picrate, 24171-66-2; **2b**, 1721-93-3; **2b** picrate, 21147-61-5; **2c**, 3297-72-1; **2c** picrate, 56947-88-7; **2d**, 7661-60-1; **2d** picrate, 79172-39-7; **2e**, 1196-39-0; **2e** picrate, 79172-40-0; **3**, 22495-79-0; 1-indanone, 480-90-0.

(4) Schröder, M. *Chem. Rev.* **1980**, *80*, 187.
(5) Sharpless, K. B.; Akashi, K. *J. Am. Chem. Soc.* **1976**, *98*, 1986. Akashi, K.; Palermo, R. E.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2063.
(6) Bosch, A.; Brown, R. K. *Can. J. Chem.* **1964**, *42*, 1718.
(7) Späth, E.; Berger, F.; Kuntara, W. *Ber.* **1930**, *63*, 134.
(8) Russell, G. A.; Weiner, S. A. *J. Org. Chem.* **1966**, *31*, 248.

Deamination of 6-Amino- and 6-(Alkylamino)-9-alkylpurines and Demethylation of Methylthiopurines by Sodium in Liquid Ammonia[1,2]

Nico J. Kos and Henk C. van der Plas*

Laboratory of Organic Chemistry, Agricultural University, Wageningen, The Netherlands

Received February 5, 1981

Several reagents have been usefully applied for the reduction of a C=N bond in purines. With sodium borohydride reduction can occur at different positions.[3-6]

(1) Part 28 on σ adducts. For part 27 see: Counotte-Potman, A.; van der Plas, H.C.; van Veldhuizen, A., submitted for publication in *J. Org. Chem.*
(2) Part 84 on pyrimidines. For part 83 see: Gönczi, C.; Swistun, Z.; van der Plas, H. C. *J. Org. Chem.* **1981**, *46*, 608.

0022-3263/81/1946-5000$01.25/0

Table I. Reaction Procedures and Yields for the Reduction of Purines

starting compd [e]	product [e]	reaction time, min	Et_2O added	yield, [a] %
6-NH_2-9-CH_3Pur	9-CH_3Pur	30	–	45
		60	–	46
		120	–	43
		30	+	40
6-NH_2-9-(2-THP)Pur	9-(2-THP)Pur	30	+	40
2',3'-*O*-isopropylideneadenosine	2',3'-*O*-isopropylidenenebularine	30	+	63 [b]
6-$NHCH_3$-9-CH_3Pur	9-CH_3Pur	30	–	42
		60	–	40
6-$N(CH_3)_2$-9-CH_3Pur	9-CH_3Pur	15	+	53
		30	+	55
2-Cl-6-NH_2-9-CH_3Pur	6-NH_2-9-CH_3Pur [c]	30	+	47
2-OCH_3-6-NH_2-9-CH_3Pur	2-OCH_3-9-CH_3Pur	30	+	60 [d]
2,6-di-NH_2-9-CH_3Pur	2-NH_2-9-CH_3Pur	30	+	60
6-SCH_3Pur	6-SHPur	10	–	40 [d]
8-SCH_3Pur	8-SHPur	5	–	100
8-SCH_3-9-CH_3Pur	8-SH-9-CH_3Pur	5	–	100

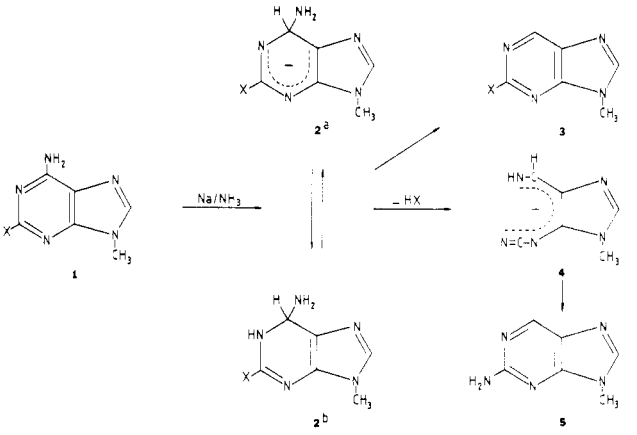
[a] Due to the small scale of the preparation, the yields were determined in duplicate by NMR spectroscopy of the reaction mixture. [b] On a larger scale (250 mg) the addition of 1 equiv of a proton donor (H_2O or EtOH) was necessary to obtain a yield of 45%. [c] Besides some 9-methylpurine. [d] For this compound the yield could not be determined by NMR spectroscopy due to the formation of byproducts. Therefore we have given the isolated yield. [e] Pur = purine, THP = tetrahydropyranyl.

When this reagent is used for the reduction of 7- or 9-alkylchloropurines, it has been reported to occur without loss of the chloro atom.[7] Treatment of thiopurines with Raney nickel catalyst gives besides desulfurization also reduction of the purine ring, yielding dihydropurines. Electrochemical methods[3,8] and hydrogenation on metal catalysts have also been applied, but the second method frequently leads to ring opening.[9] Sodium in liquid ammonia as a reducing agent in purine chemistry has been reported for removing benzyl groups from *N*- and *S*-benzylpurines.[3]

Results and Discussion

We found that on treatment of 6-amino-9-methylpurine (**1**, X = H) with sodium in liquid ammonia and subsequent addition of ammonium sulfate (to quench the reaction mixture) 9-methylpurine (**3**, X = H) was obtained in a yield of about 45% (Table I, Scheme I). This yield was not improved by increasing the reaction time, by addition of the proton donor ethanol, or by using tetrahydrofuran or ether as a cosolvent, although with ether less byproducts are formed. Replacement of sodium by lithium or potassium gave inferior results. This simple method to replace the amino group at position 6 in 9-alkylpurines by a hydrogen atom is synthetically useful, since up to now deamination could only be effected by treatment with *n*-pentyl nitrite.[10] We assume that the first step in the conversion of **1** (X = H) into **3** (X = H) involves reduction of the N(1)–C(6) bond to give as intermediate the anion of 1,6-dihydropurine (**2a**, X = H) or its conjugate acid (**2b**, X = H). Loss of the amide ion from **2a** (X = H) or ammonia from **2b** (X = H) yields **3** (X = H) (Scheme I).[11]

Scheme I



There is direct evidence for the presence of **2** (X = H), since the ^1H NMR spectrum of the solution prior to quenching showed a triplet at δ 5.62 (J = 7 Hz) for H(6); this chemical shift is comparable to that of δ 5.75 for H(6) in **6** (X = H) (Scheme II), the adduct being formed by addition of an amide ion to the anion of 2-X-purine.[12]

The upfield shifts of the signals for H(2) in **2**(X = H) [H(2) in **1** (X = H) shifts from δ 7.72 to 7.08 in **2** (X = H)] and H(8) [H(8) in **1** (X = H) shifts from δ 7.68 to 7.01 in **2** (X = H)] are also in agreement with the formation of intermediate **2** (X = H).[12] The signals were assigned by comparison with the spectra of 6-amino-8-deuterio-9-methylpurine. These results show clearly that the deamination reaction proceeds via a reduction of the N(1)–C(6) bond followed by elimination. The elimination reaction takes place on quenching with ammonium sulfate; it explains why **3** (X = H) can be isolated in reasonable yield, although this compound is not stable in liquid ammonia containing potassium amide.

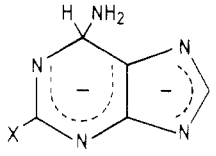
The successful deamination of **1** (X = H) to **3** (X = H) induced us to investigate the scope of this reaction. Adenine was found to be unreactive; apparently the presence of an alkyl group at position 9 is necessary for a successful deamination.[13] However, when we reacted 6-amino-9-

(3) For a review: Lister, J. H. In "The Chemistry of Heterocyclic Compounds, Fused Pyrimidines, Part II"; Brown, D. J., Ed.; Wiley: New York, 1971.
(4) Hecht, S. M.; Adams, B. L.; Kozarich, J. W. *J. Org. Chem.* **1976**, *41*, 2303.
(5) Adams, B. L. In "Nucleic Acid Chemistry"; Townsend, L. B., Tipson, R. S., Eds.; Wiley: New York, 1978; Vol. 2, p 615.
(6) Maki, Y.; Suzuki, M.; Ozeki, K. *Tetrahedron Lett.* **1976**, 1199.
(7) Neiman, Z. *Experientia* **1979**, *35*, 1418.
(8) Santhanam, K. S. V.; Elving, P. *J. Am. Chem. Soc.* **1974**, *96*, 1653.
(9) Wegner, M. M.; Rapoport, H. *J. Org. Chem.* **1977**, *42*, 3065.
(10) Nair, V.; Richardson, S. G. *J. Org. Chem.* **1980**, *45*, 3969.
(11) This behavior is comparable to the loss of HBr from 1,6-dihydro-6-bromopurine, of H_2O from 1,6-dihydro-6-hydroxypurine,[3] and of ammonia from 1,2,3,6-tetrahydroadenine.[8]
(12) Kos, N. J.; van der Plas, H. C.; van Veldhuizen, A. *J. Org. Chem.* **1979**, *44*, 3140.

(2-tetrahydropyranyl)purine with sodium in liquid ammonia, 9-(2-tetrahydropyranyl)purine was obtained.[14]

We also found that deamination of adenosine into nebularine does not occur but that the reductive removal of the amino group from 2',3'-*O*-isopropylideneadenosine into 2',3'-*O*-isopropylidenebularine easily takes place.[15] Reductive removal is not confined to the amino group: Substituted amino groups are also easily replaced by hydrogen; reduction of 6-(methylamino)-9-methylpurine and 6-(dimethylamino)-9-methylpurine gave 9-methylpurine. The direct replacement of a substituted amino group by hydrogen has not been described before, since diazotization[10] cannot be applied with substituted amino groups.

From our amination studies with purines[16] containing a leaving group at position 2, it has been established that these compounds undergo initial adduct formation at position 6, yielding a 6-amino-1,6-dihydropurine (**6**, X = Cl, F, SCH_3). This adduct undergoes a ring-opening re-



6

action, leading to an open-chain intermediate that gives ring closure into 2-aminopurine [S_N(ANRORC) mechanism]. Since in this paper it has been shown that a 6-amino-1,6-dihydropurine can also be obtained by reduction of a 6-aminopurine, we became interested in the behavior of 6-aminopurines containing a leaving group at position 2, i.e., **1**.

It is possible that on reduction of compound **1** intermediate **2** is formed which then may undergo a ring opening into **4**; ring closure affords 2-amino-9-methylpurine (**5**; **1** → **2** → **4** → **5**; Scheme I). On treatment of 6-amino-2-chloro-9-methylpurine (**1**, X = Cl) with sodium in liquid ammonia, it was observed that the halogen atom was quickly lost, giving 6-amino-9-methylpurine, which yielded on further reduction 9-methylpurine. Reduction of 6-amino-2-methoxy-9-methylpurine (**1**, X = OCH_3) gave 2-methoxy-9-methylpurine (**3**, X = OCH_3) as the sole product. No trace of 2-amino-9-methylpurine (**5**) was found. The conclusion is evident: no ring opening has occurred, only elimination of amide ion (**1** → **2** → **3**; X = OCH_3). It is interesting that reduction of 2,6-diamino-9-methylpurine (**1**, X = NH_2) selectively removes the amino group from position 6, yielding 2-amino-9-methylpurine [**3** (X = NH_2) = **5**]. This product is very likely formed via elimination of ammonia from N(1)–C(6) via route **1** → **2** → **3** (X = NH_2). All the results mentioned before clearly indicate that it is the amino group at position 6 and not at position 2 which can be reductively removed.

Attempts to perform reductive removal of methoxy and methylthio groups[17] from position 6 in 9-methylpurines failed; 6-methoxy-9-methylpurine and 6-(methylthio)-9-methylpurine could not be converted into 9-methylpurine. However, 8-(methylthio)-9-methylpurine was found to undergo an S-demethylation into 7,8-dihydro-8-thio-9-methylpurine (Table I). This reaction proceeded quickly and quantitatively. Also 6-(methylthio)purine and 8-(methylthio)purine could successfully be demethylated. These reactions are of preparative interest since a similar conversion has only been effected in a few cases with hydrogen sulfide or phosphorus pentasulfide.[3]

Experimental Section

^{1}H NMR spectra were obtained with a Varian EM-390 or a Hitachi Perkin-Elmer R-24B (60 MHz) with Me_4Si as an internal standard. When measurements were made in liquid ammonia, the sample temperature was ca. −50 °C, and NH_3 was used as the standard. The spectra were converted to the Me_4Si scale by adding 0.95 ppm. Mass spectra and ^{15}N contents were determined on an AEI MS-902 mass spectrometer. UV spectra were obtained with a Beckman Acta C III and a Perkin-Elmer 550. Melting points are uncorrected.

Preparation of Starting Materials. 6-(Methylthio)purine and 8-(methylthio)purine are commercially available. 6-Amino-9-methylpurine,[18] 6-(methylamino)-9-methylpurine,[19] 6-(dimethylamino)-9-methylpurine,[19] 6-amino-9-(2-tetrahydropyranyl)purine,[20] 2',3'-*O*-isopropylideneadenosine,[21] 6-amino-2-chloro-9-methylpurine,[22] 6-(methylthio)-9-methylpurine,[23] 6-methoxy-9-methylpurine,[19] and 8-(methylthio)-9-methylpurine[24] were prepared according to procedures as described in the literature.

6-Amino-8-deuterio-9-methylpurine was obtained by refluxing 6-amino-9-methylpurine in an excess of deuterium oxide.[25] Deuterium was incorporated (95%) at position 8, as established by ^{1}H NMR spectroscopy.

9-Methylpurine (3, X = H). Methylation of purine with tetramethylammonium hydroxide gave a mixture of 7- and 9-methylpurine.[18] Separation by column chromatography on silica gel by using 10% methanol in chloroform as eluant gave 7-methylpurine (yield 24%) and 9-methylpurine (12%).

2,6-Diamino-9-methylpurine (1, X = NH_2).[26] Method I. 2,6-Dichloro-9-methylpurine was heated with ethanolic ammonia in a sealed tube for 24 h at 160 °C. The residue obtained after evaporation of the reaction mixture in vacuo was washed with water and purified by column chromatography on silica gel with 15% of methanol in chloroform as eluant to yield 50% (recrystallized from water) of the product. Anal. Calcd for $C_6H_8N_6$: C, 43.89; H, 4.91. Found: C, 44.12; H, 4.97.

Method II. Methylation of 2,6-diaminopurine with tetramethylammonium hydroxide and sublimation at 260 °C (0.06 mm)[18] gave, after purification by column chromatography, 2,6-diamino-9-methylpurine, yield 30%.

6-Amino-2-methoxy-9-methylpurine (1, X = OCH_3). Sublimation of 6-amino-2-methoxypurine with tetramethylammonium hydroxide [260 °C (0.06 mm)][18] gave a reaction mixture that after purification by column chromatography (silica gel, 10% methanol in chloroform) gave in a yield of 20% **1** (X = OCH_3), being identical with the product prepared according to the procedure described in the literature.[27]

General Reduction Procedure. A 15-mL sample of dry liquid ammonia (distilled from potassium) was condensed, and, if necessary, 10 mL of diethyl ether was added. The starting material

(13) This result is in agreement with literature data describing the debenzylation of some 6-aminopurines without loss of the amino group.[3]

(14) Subsequent acid hydrolysis provides the principle of a route from adenine to purine (Sutcliffe, E. Y.; Robins, R. K. *J. Org. Chem.* **1963**, *28*, 1662; Skoog, F.; et al. *Phytochemistry* **1967**, *6*, 1169). The benzyl group cannot be used for this purpose.[13]

(15) Removal of the isopropylidene group provides a route from adenosine to nebularine (Reese, C. B. In "Protective Groups in Organic Chemistry"; McOmie, J. F. W., Ed.; Plenum Press: London, 1973). The acetyl or benzoyl group cannot be used since these are removed under the reaction conditions to give adenosine.

(16) Kos, N. J.; Van der Plas, H. C. *J. Org. Chem.* **1980**, *45*, 2942.

(17) Sodium in liquid ammonia is used to debenzylate benzylthiopurines,[3] but it is known that in other compounds methylthio groups can be demethylated in this way (House, H. O. "Modern Synthetic Reactions"; W. A. Benjamin: New York, 1972).

(18) Myers, T. C.; Zeleznick, L. *J. Org. Chem.* **1963**, *28*, 2087.

(19) Robins, R. K.; Lin, H. H. *J. Am. Chem. Soc.* **1957**, *79*, 490.

(20) Robins, R. K.; Godefroi, E. F.; Taylor, E. C.; Lewis, L. R.; Jackson, A. *J. Am. Chem. Soc.* **1961**, *83*, 2574.

(21) Hampton, A.; Margrath, D. I. *J. Am. Chem. Soc.* **1957**, *79*, 3250. Baddiley, J. *J. Chem. Soc.* **1951**, 1348.

(22) Falconer, R.; Gulland, J. M.; Story, L. F. *J. Chem. Soc.* **1939**, 1784.

(23) Brown, D. J.; Ford, P. W. *J. Chem. Soc. C* **1969**, 2620.

(24) Badger, R. J.; Barlin, G. B. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1854. Brown, D. J.; Mason, S. F. *J. Chem. Soc.* **1957**, 682.

(25) Maeda, M.; Kawazoe, Y. *Tetrahedron Lett.* **1957**, 1643.

(26) Taylor, E. C.; Beardsley, G. P.; Maki, Y. *J. Org. Chem.* **1971**, *36*, 3211.

(27) Sepiol, J.; Kazimierczuk, Z.; Shugar, D. *Z. Naturforsch., C.: Biosci.* **1976**, *31*, 361.

(50 mg) was introduced with stirring. Small pieces of sodium were added to maintain a blue color during the reaction. The reaction mixture was quenched with ammonium sulfate, the ammonia was evaporated, and the residue was extracted with a mixture of chloroform and methanol. Separation of the products could be achieved by column chromatography or preparative TLC with mixtures of chloroform and methanol as the eluant. All reaction products which were formed and isolated were known compounds except 2-methoxy-9-methylpurine (3, X = OCH_3), mp 140.5–142.5 °C. Its structure was proven by ^1H NMR (Me_2SO-d_6) [δ 3.72 (s, NCH_3), 3.93 (s, OCH_3), 8.26 (s), 8.79 (s)], by comparison of the UV spectrum with that of 2-ethoxy-9-methylpurine[28] (pH 1, λ_{max} = 282 nm; pH 7, λ_{max} = 280 nm), and by mass spectroscopy (exact mass calcd for $C_7H_8N_4O$ m/e 164.0698, found m/e 164.0703).

Acknowledgment. We are indebted to Drs. C. A. Landheer and Mr. W. P. Combé for the mass spectroscopic data, to Mr. A. van Veldhuizen for measuring some NMR spectra, and to Mr. H. Jongejan for carrying out the microanalyses.

Registry No. 6-NH_2-9-CH_3Pur, 700-00-5; 6-NH_2-9-(2-THP)Pur, 7306-67-4; 2′,-3′-*O*-isopropylideneadenosine, 362-75-4; 6-$NHCH_3$-9-CH_3Pur, 2009-52-1; 6-$N(CH_3)_2$-9-CH_3Pur, 3013-82-9; 2-Cl-6-NH_2-9-CH_3Pur, 7013-21-0; 2-OCH_3-6-NH_2-9-CH_3Pur, 61494-91-5; 2,6-di-NH_2-9-CH_3Pur, 30720-65-1; 6-SCH_3Pur, 50-66-8; 8-SCH_3Pur, 33426-53-8; 8-SCH_3-9-CH_3Pur, 24851-51-2; 9-CH_3Pur, 20427-22-9; 9-(2-THP)Pur, 16347-32-3; 2′,3′-*O*-isopropylidenenebularine, 67604-85-7; 2-OCH_3-9-CH_3Pur, 79069-17-3; 2-NH_2-9-CH_3Pur, 5752-08-9; 6-SHPur, 50-44-2; 8-SHPur, 583-40-4; 8-SH-9-CH_3-Pur, 74537-62-5; 7-methylpurine, 18346-04-8; 2,6-dichloro-9-methylpurine, 2382-10-7; 2,6-diaminopurine, 1904-98-9; 6-amino-2-methoxypurine, 28128-30-5.

(28) Barlin, G. B. *J. Chem. Soc. B* **1967**, 954.

X-ray Analysis, Molecular Structure, and Nuclear Magnetic Resonance Spectra of the Second Dimer from Thermal Rearrangement of 1,1-Dichloro-2,5-diphenylcyclopropabenzene: (*Z*)-2,2′,3,3′-Tetrachloro-4,4′,7,7′-tetraphenyl-1,1′-bicycloheptatrienylidene

Ward T. Robinson* and Evert J. Ditzel

Department of Chemistry, University of Canterbury, Christchurch 1, New Zealand

Helmut M. Hügel and David P. Kelly*

Department of Organic Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

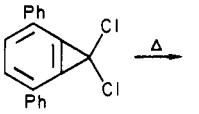
Brian Halton*

Department of Chemistry, Victoria University of Wellington, Private Bag, Wellington, New Zealand

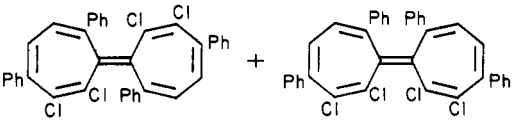
Received June 5, 1981

Introduction

We have recently reported the crystallographic analysis of a pale yellow dimer A, $C_{38}H_{24}Cl_4$, produced from thermal decomposition of 1,1-dichloro-2,5-diphenylcyclopropabenzene (1) in either acetone or benzene.[1,2] This dimer was shown to have the novel cycloheptatrienylidene (heptafulvalene) structure **2** in which the two seven-membered rings are bent up facing each other in a "U" shape. The puckering of these rings and the parallel arrangement of the two halves of the molecule result in spectroscopic properties quite unlike those expected from a planar, conjugated cycloheptatrienylidene structure.[3] The most likely pathway for the conversion **1** → **2** has been discussed.[2]



1



pale yellow dimer A **2** bright yellow dimer B **3**

Table I. Crystal Data

formula	$C_{38}H_{24}Cl_4$	$a = b$ 17.530 (2) Å
mol wt	622.427	c 36.611 (9) Å
space group	$I4_1/acd$	
$\rho_x(16C_{38}H_{24}Cl_4/\text{cell})$	1.36 g cm^{-3}	

The second, "bright yellow dimer B", is produced concurrently with and was separated manually from **2**.[1,2] The spectroscopic properties of the two dimers were almost identical except for subtle differences in their ^1H spectra, and consequently it was not possible to distinguish between a conformational and a configurational isomer of **2** as the structure for dimer B.[2] We now report the X-ray analysis and determination of the molecular structure of the bright yellow dimer B, which is in fact the *Z* isomer **3** but with the two seven-membered rings in an anti orientation to one another. Rationalization of the spectroscopic data obtained at 23.5 kG is now possible.

X-ray Analysis

Experimental Methods. Both dimers were recrystallized from acetone and a specimen (0.48 × 0.95 × 1.58 mm) of the bright yellow dimer B was chosen for study. From the diffraction symmetry and systematic absences, the space group was deduced as $I4_1/acd$. Unit cell parameter (Table I) and intensity data were obtained by using Zr filtered Mo Kα radiation (λ = 0.7107 Å) on a Hilger and Watts four-circle diffractometer. Data reduction yielded 2125 unique reflections, which were not corrected for absorption or polarization.

Application of conventional heavy atom methods, difference Fourier syntheses and full-matrix least-squares calculations were used to complete and refine the model. Final least-squares refinement cycles were performed with 98 variables and the 1193 data with $|F_o^2| > 3\sigma(F_o)^2$. Standard atomic scattering factors[4] were used and shifts in the atomic parameters on the last cycle were $<0.06\sigma$. At convergence a conventional R factor of 0.080 was obtained. A final difference Fourier map showed peaks due to hydrogen atoms, the highest of these being one-third the height of the least carbon atom peak. Tabulations of the final positional and thermal parameters and a listing of the observed and calculated structure factors are available as supplementary material.

(1) Hügel, H. M.; Kelly, D. P.; Browne, A. R.; Halton, B.; Milsom, P. J.; Woolhouse, A. D. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2340–2342.
(2) Fahey, J. A.; Hügel, H. M.; Kelly, D. P.; Halton, B.; Williams, G. J. B. *J. Org. Chem.* **1980**, *45*, 2862–2865.
(3) Meyers, J. A.; Joines, R. C.; Jones, W. M. *J. Am. Chem. Soc.* **1970**, *92*, 4740–4742.
(4) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17–23. Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321–324.
(5) Johnson, C. K. Report ORNL 3794; Oak Ridge National Laboratory: Oak Ridge, TN.

0022-3263/81/1946-5003$01.25/0