distilling flask, but no 5-methoxyindene was detectable in this residue.

To ascertain the importance of potassium bisulfate to this isomerization, authentic samples of IV and XI were allowed to distil at bath temperatures of 220–240° for 30 min. both in the presence and in the absence of potassium bisulfate. The results in all cases were the same. The distillate was a mixture of the starting material and its isomer. Only the isomer originally present could be detected in the residue. It thus appears that any synthesis of 5- or 6-methoxyindene which involves distillation of the final product at atmospheric pressure will lead to mixtures of the two isomers. The results of previous workers[2,12] may be explained on this basis.

Experimental

General.—Melting points were taken on a Kofler micro hot-stage apparatus (A. H. Thomas Co.) and are corrected. Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer. Ultraviolet spectra were recorded on a Beckman Model DB spectrophotometer. N.m.r. spectra were obtained with a Varian A-60 high resolution n.m.r. spectrometer. The samples were run in carbon tetrachloride solution using tetramethylsilane as an internal reference standard and the chemical shifts are reported as τ values. Microanalyses were performed by the Galbraith Laboratories, Inc., Knoxville 21, Tenn. Thin layer chromatograms were run on silica gel G and aluminum oxide G (both from Research Specialties Co., Richmond, Calif.) with benzene–carbon tetrachloride (1:1). The spots were located with a spray made by mixing 0.2 ml. of a 37% solution of formaldehyde with 10 ml. of concentrated sulfuric acid.[17] With this developing agent, 5-methoxyindene gave a blue-green color while 6-methoxyindene gave a purple-violet color.

6-Methoxy-1-indanone (II).—This ketone was prepared according to Bone and Cort.[15] The polyphosphoric acid was prepared by dilution of 500 g. of commercial polyphoshoric acid (82–84% P_2O_5) with 120 g. of 85% phosphoric acid. II was obtained as white needles in 27% yield, m.p. 109–111° (lit.[15] m.p. 108–109).

6-Methoxy-1-indanol (III).—A solution of 2.5 g. (0.015 mole) of II in 176 ml. of dry ether was heated under reflux for 1 hr. with 0.27 g. of lithium aluminum hydride. The mixture was cooled, excess $LiAlH_4$ was destroyed with water, and the mixture was filtered through Celite. The filtrate was dried with sodium sulfate and the solvent was removed to yield a clear, slightly yellow liquid which gives a white solid (2.4 g., 95%) after storage overnight at −15° under nitrogen. Crystallization from *n*-hexane gives white crystals of 6-methoxy-1-indanol (2.1 g., 81%), m.p. 47–48.5°.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.21; H, 7.34.

5-Methoxyindene (IV).—A solution of 2.5 g. (0.015 mole) of III in 73 ml. of dry benzene was heated under reflux for 30 min. with 0.2 g. of *p*-toluenesulfonic acid. The mixture was cooled, water was added, and the phases were separated. The water phase was extracted with ether. All organic phases were combined and dried with sodium sulfate, and the solvent was removed to give a tan liquid (2.3 g., 100%). Distillation at 110–145° (10 mm.) yielded 5-methoxyindene as a colorless liquid (1.2 g., 54%): infrared (liquid film) 1550, 1118, 1107, 1070, 948, 843, 730, 639 cm.$^{-1}$; λ_{max} (absolute ethanol) 252 mμ (log ϵ 3.69); n.m.r. τ 7.83 (methylene protons), 6.40 (methoxy protons), 3.68–2.69 (vinyl protons overlapping aromatic protons). IV was homogenous on thin layers of silica gel or alumina with R_f 0.63 and 0.93, respectively.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 81.81; H, 6.79.

5-Methoxy-1-indanone (VI). Method A.—The ketone was prepared as directed by Bone and Cort.[15] The polyphosphoric acid was prepared as in the synthesis of II. VI was obtained as white crystals in 26% yield, m.p. 109–110.5°. (lit.[15] m.p. 108°).

Method B.—The ketone was prepared according to the method of Panetta and Bunce.[12,19] The product had m.p. 110–110.5° (lit.[12] m.p. 108.4–109.4°). The infrared spectrum of this product was identical with the ketone produced by method A. A mixture melting point of the two products showed no depression.

5-Methoxy-1-indanol (X).—A solution of 4.8 g. (0.028 mole) of VI was heated under reflux in 340 ml. of dry ether with 1.0 g. of lithium aluminum hydride. The 5-methoxy ketone was found to be more resistant to reduction than was the 6-methoxy ketone, the former requiring 4 hr. for complete reduction. The reaction mixture was then treated as described for 6-methoxy-1-indanol. The crude product contained no 6-methoxyindene, but distillation at 115–140° (0.02 mm.) gave 5-methoxy-1-indanol which was contaminated with the indene.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 75.42; H, 7.37.

6-Methoxyindene (XI).—A solution of 1.59 g. (0.097 mole) of X was heated under reflux in 47 ml. of dry benzene for 30 min. with 0.13 g. of *p*-toluenesulfonic acid. The mixture was then treated as above for 5-methoxyindene to yield a thick, yellow liquid (1.53 g., 96%). This was dissolved in petroleum ether (b.p. 30–60°) and cooled to −15° under nitrogen. After 2 days a white solid separated. Three recrystallizations from petroleum ether gave pure 6-methoxyindene (0.49 g., 32%): m.p. 46–47°; infrared (Nujol) 1093, 875, 823, 738 cm.$^{-1}$; λ_{max} (absolute ethanol) 268 mμ (log ϵ 4.02); n.m.r. τ 6.87 (methylene protons), 6.35 (methoxy protons), 3.65–2.85 (vinyl protons overlapping aromatic protons, definitely different from the corresponding pattern in IV). XI was homogeneous on thin layers of silica gel and alumina with R_f 0.28 and 0.84, respectively.

Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.01; H, 6.69.

Attempted Isomerization of 5- and 6-Methoxyindene.—Indene solutions (2 *M*) in pyridine were treated with 1.08 *M* triethylamine as catalyst at 26–28° for 4 days. Periodically, aliquots were removed and chromatographed on silica gel. No isomerization could be detected.

Acknowledgment.—The authors wish to express their appreciation to Dr. A. J. Solo of the State University of New York at Buffalo for helpful discussions regarding this work.

(19) W. S. Johnson, J. M. Anderson, and W. E. Shelberg, *J. Am. Chem Soc.*, **66**, 218 (1944).

Methylation of Simple Unsaturated Hydrocarbons by Dimethyl Sulfoxide

P. A. ARGABRIGHT, J. E. HOFMANN,[1] AND A. SCHRIESHEIM

Process Research Division,
Esso Research and Engineering Company, Linden, New Jersey

Received April 8, 1965

Although dimethyl sulfoxide (DMSO) has been used extensively as a solvent medium, it is only quite recently that it has been recognized that the DMSO itself participates in a number of base-catalyzed reactions. The hydrogens are quite labile, and exchange between these and weak organic acids is readily measured.[2] Preparation of the methylsulfinyl carbanion was reported by Corey.[3] The addition of this carbanion to various unsaturated bonds has been ob-

(1) To whom correspondence should be addressed.

(2) (a) A. Schriesheim, J. E. Hofmann, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **83**, 3731 (1961); (b) J. E. Hofmann, R. J. Muller, and A. Schriesheim, *ibid.*, **85**, 3000, 3002 (1963).

(3) E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 866 (1962).

served by Russell,[4] Corey,[5] and Walling.[6] In some cases the product of addition undergoes subsequent elimination of the CH_3SO moiety. The case for this latter reaction has been well documented by elimination studies that have been carried out at this laboratory.[7] In the present work it has been found that dimethyl sulfoxide, under the influence of base, reacts with a number of simple unsaturated hydrocarbons. The net result of this reaction is the production of methylated analogs of the starting hydrocarbon.

Results

The products from reaction of dimethyl sulfoxide with a number of diolefin and aromatic hydrocarbons are shown in Table I. All of this work employed DMSO as both the reactant and solvent. When DMSO is used in reagent quantities, employing 0.6 *M* potassium *t*-butoxide in diglyme as the solvent media, a similar reaction takes place, but the yield of isomeric pentadienes from butadiene is only 13% in 95 hr. Dimethyl sulfone proves to be slightly more effective in diglyme solution; a 37% yield is achieved in 88 hr.

TABLE I

Reactant	Time, hr.	Yield, mole %	Product(s)
Butadiene	1	50[a]	80% *trans*-1,3-pentadiene 20% *cis*-1,3-pentadiene
1,3-Pentadiene[b]	17	40[a]	Isomeric hexadienes[c]
Anthracene	1	55	82% 9-methylanthracene 18% 9,10-dimethylanthracene
Naphthalene	92	15	96% 1-methylnaphthalene 4% 2-methylnaphthalene
1,3-Cyclohexadiene	24	10	See footnote *d*
1,3-Cyclooctadiene	95	0	...
Norbornadiene	264	0	...
Benzene	100	0	...

[a] Mass spectrometric analysis indicates the presence of traces of higher molecular weight diolefinic analogs. [b] 80% *trans*, 20% *cis*. [c] Upon hydrogenation this material contained 23% 2-methylpentane and 77% *n*-hexane. [d] The material is a complex mixture which probably contains methylcyclohexanes, methylcyclohexadienes, and toluene.

Discussion

Based on existing information[3-7] a fairly simple mechanism can be evolved for the methylation reaction (reactions 1 through 5 using butadiene as an example).

$$CH_3SOCH_3 + t\text{-BuO} \rightleftharpoons CH_3SOCH_2^- + t\text{-BuOH} \quad (1)$$

$$CH_3SOCH_2^- + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow CH_3SOCH_2CH_2\overset{\delta-}{C}H{=}CH{=}\overset{\delta-}{C}H_2 \quad (2)$$

$$CH_3SOCH_2\overset{\delta-}{C}H_2CH{-}CH{-}\overset{\delta-}{C}H_2 + BH \longrightarrow CH_3SOCH_2CH_2CH{=}CHCH_3 + B^- \quad (3)$$

$$CH_3SOCH_2CH_2CH{=}CHCH_3 + B^- \longrightarrow CH_3SOCH_2^-CHCH{=}CH{-}CH_3 + BH \quad (4)$$

$$CH_3SO{-}CH_2{-}\overset{-}{C}H{-}CH{=}CH{-}CH_3 \longrightarrow CH_2{=}CH{-}CH{=}CH{-}CH_3 + CH_3{-}SO \quad (5)$$

It is conceivable that the intermediate formed in reaction 2 could undergo direct elimination to form either cyclopentene or vinylcyclopropane. (This would be analogous to the formation of diphenylcyclopropane from diphenylethylene which was found by Corey[5] and Walling.[6]) However, neither of these products was observed. Since cyclopentene and similar cyclopropane compounds are stable in KO-*t*-Bu–DMSO, it is concluded that this reaction does not occur with the simple diolefins. No other intermediates, such as that formed in reaction 3, were found in the reaction product, and material balance of reactant and products was sufficiently good to rule out any large quantities of these materials. This would indicate that elimination, reactions 4 and 5, is fairly rapid, and this is consistent with our previously mentioned elimination studies.[7]

When 1,3-pentadiene is employed as the reactant, initial addition of the methylsulfinyl carbanion occurs at both the 1- and 4-positions. However, analysis of the hydrogenation product indicates a preference of about 3:1 for the 1-position. As expected, the addition to anthracene was very rapid and the initial product undergoes further reaction to yield the dimethyl derivative. Naphthalene is quite unreactive and benzene itself undergoes no measurable reaction even when the temperature is increased to 80°. With the cyclodienes, cyclohexadiene undergoes a small amount of reaction while norbornadiene and cyclooctadiene are unreactive.

It is quite apparent that the relative order of reactivities is controlled by the stability of the anion formed during the addition step, reaction 1. This is identical with the situation that exists during base-catalyzed hydrogen transfer[8] where transfer of hydride to the acceptor molecule, *i.e.*, butadiene or anthracene, is rate determining. Thus, the initial carbanion from anthracene would have enhanced stability over that from butadiene, and cyclohexadiene in turn would be less reactive than butadiene. Preferential substitution at the 1-position in naphthalene occurs because of the greater resonance energy associated with the ion in the β-position rather than the α-position. Benzene, norbornadiene, and cyclooctadiene are unreactive because reaction 1 is energetically unfavorable. For benzene this would mean disrupting the aromaticity, while in cyclooctadiene it is difficult for the allylic system to become planar. With the norbornadiene it was thought that a nortricyclene derivative might be formed but such was not observed. The fact that dimethyl sulfone is more reactive than dimethyl sulfoxide is probably due to the enhanced acidity of the α-hydrogens on the sulfone.

No attempt has been made to isolate or analyze the sulfur-containing products formed during the elimination step. These materials undoubtedly undergo further reaction leading to a rather complex mixture. An unfortunate outcome of this is neutralization of the base, and systems undergoing elimination rapidly become unreactive.

These data not only give evidence for the reactivity of dimethyl sulfoxide toward unsaturated hydrocarbons, but also point out its usefulness as a novel methylating agent. Presumably other sulfoxides and sulfones could be used in a similar manner.

(4) G. A. Russell, E. G. Janzen, H. D. Becker, and F. J. Smentowski, *J. Am. Chem. Soc.*, **84**, 2652 (1962).

(5) M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, **28**, 254 (1963).

(6) C. Walling and L. Bollyky, *ibid.*, **28**, 256 (1963).

(7) (a) J. E. Hofmann, T. J. Wallace, P. A. Argabright, and A. Schriesheim, *Chem. Ind.* (London), 1243 (1963); (b) T. J. Wallace, J. E. Hofmann, and A. Schriesheim, *J. Am. Chem. Soc.*, **85**, 2739 (1963); (c) J. E. Hofmann, T. J. Wallace, and A. Schriesheim, *ibid.*, **86**, 1561 (1964).

(8) J. E. Hofmann, P. A. Argabright, and A. Schriesheim, *Tetrahedron Letters*, **17**, 1005 (1964).

Experimental

Reagents.—Potassium *t*-butoxide was obtained from Mine Safety Appliances, Inc., as the sublimed powder. Analyses indicated a minimum purity of 98.5 wt. %, the major impurity being K_2CO_3. Dimethyl sulfoxide was obtained from Crown-Zellerbach. The material was freshly distilled from Linde 13X Molecular Sieves before use. The hydrocarbons were obtained from Matheson Coleman and Bell (reagent grade), as was dimethyl sulfone. Diglyme (dimethyl ether of diethylene glycol), obtained from Matheson Coleman and Bell, was distilled from Linde 13X Molecular Sieves before use.

Procedure.—The reactions were carried out by contacting 3 mmoles of the olefinic or aromatic hydrocarbon with 7.0 ml. of a 0.6 *M* solution of potassium *t*-butoxide in dimethyl sulfoxide. All reaction mixtures were prepared in a nitrogen drybox and carried out in a thermostated bath at 55 ± 0.2°. Reaction product analyses were performed by gas chromatography (comparing relative retention volumes with those of authentic samples) and mass spectrometry.

The Use of the Allyl Group as a Blocking Group for the Synthesis of N-Substituted Purines[1]

JOHN A. MONTGOMERY AND H. JEANETTE THOMAS

Kettering-Meyer Laboratory, Southern Research Institute, Birmingham, Alabama

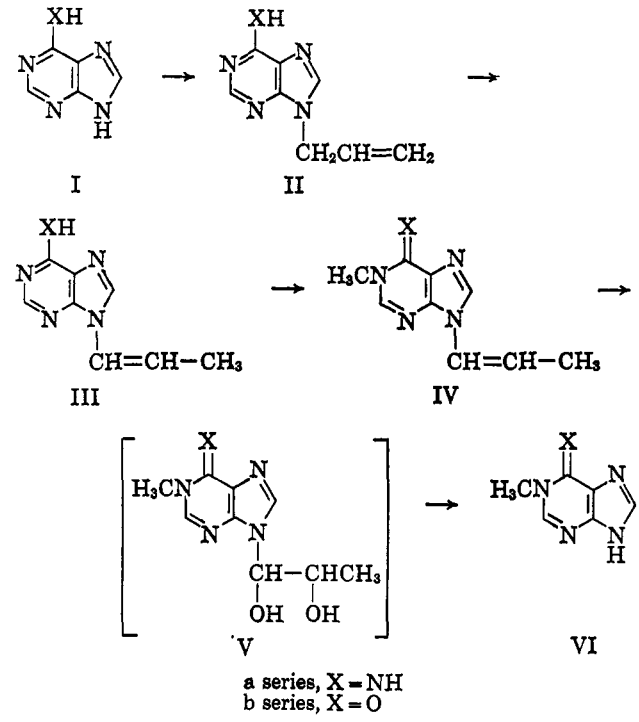
Received April 30, 1965

It has been amply demonstrated that the position of alkylation[2,3] or sugar coupling[2,4] of purines can be controlled by N substitution of purines by removable blocking groups. Thus the ribose moiety has been useful in the preparation of 1-substituted purines[2,5,6] and the benzyl group has been used to prepare both 1- and 7-substituted purines.[2-4] The use of the ribose blocking group is limited, practically, to cases in which one can utilize naturally occurring ribonucleosides as starting materials, and even then the method leaves something to be desired, since the acid cleavage of the ribose moiety results in sugar decomposition products that often make the isolation of the desired purine difficult and the yield low. The use of the benzyl group avoids most of these problems, but catalytic hydrogenolysis of the benzyl group is usually difficult and slow.[2] In some cases ring reduction occurs as readily as removal of the benzyl group resulting in low yields of the desired purines.[7] The benzhydryl group[8] is apparently not significantly better in this regard.[7]

In a search for a better blocking group, and one whose removal is compatible with the acidic lability of purine nucleosides, we turned to the allyl group since it has been shown that allyl ethers are facilely rearranged by means of potassium *t*-butoxide in dimethyl sulfoxide to propenyl ethers[9] that can be oxidatively cleaved under mild conditions at a basic pH.[10]

To test the potential of this procedure applied to purines, 9-allyladenine (IIa) was prepared by the alkylation of adenine (I) with allyl bromide in N,N-dimethylacetamide in the presence of potassium carbonate.[11] Treatment of 9-allyladenine (IIa) with potassium *t*-butoxide in dimethyl sulfoxide gave a good yield of 9-propenyladenine (IIIa), which was alkylated with methyl iodide to give 1-methyl-9-propenyladenine (IVa) hydriodide. Treatment of IVa with potassium permanganate under basic conditions presumably resulted in hydroxylation of the double bond, but this intermediate (Va) was not stable to the conditions of the reaction and 1-methyladenine (VIa)[14] was obtained directly in good yield. Since it is well known that 1-substituted adenines can rearrange to N^6-substituted adenines under basic conditions, the absence of N^6-methyladenine in VIa was established by means of thin layer chromatography.

The same sequence of reactions was applied to 9-allylhypoxanthine (IIb) and again a good yield of 1-methylhypoxanthine (VIb) was readily obtained. The preparation of 7-substituted purines from 3-allylpurines by this procedure is currently under investigation. Possible applications of this procedure to other nitrogen heterocycles is obvious.



Experimental

The melting points reported were determined on a Kofler Heizbank and are corrected. The ultraviolet spectra were de-

(1) This work was supported by funds from the C. F. Kettering Foundation and the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institutes of Health, Contract No. PH-43-64-51.

(2) J. A. Montgomery and H. J. Thomas, *J. Org. Chem.*, **28**, 2304 (1963).

(3) N. J. Leonard and T. Fujii, *J. Am. Chem. Soc.*, **85**, 3719 (1963); *Proc. Natl. Acad. Sci. U. S.*, **51**, 73 (1964).

(4) J. A. Montgomery and H. J. Thomas, *J. Am. Chem. Soc.*, **85**, 2672 (1963).

(5) E. Shaw, *ibid.*, **80**, 3899 (1958).

(6) R. W. Balsiger, A. L. Fikes, T. P. Johnston, and J. A. Montgomery, *J. Org. Chem.*, **26**, 3446 (1961).

(7) J. A. Montgomery and H. J. Thomas, unpublished observations.

(8) J. A. Montgomery and H. J. Thomas, *J. Heterocyclic Chem.*, **1**, 115 (1964).

(9) C. C. Price and W. H. Snyder, *J. Am. Chem. Soc.*, **83**, 1773 (1961).

(10) J. Cunningham, R. Gigg, and C. D. Warren, *Tetrahedron Letters*, 1191 (1964).

(11) In the absence of base the allylation takes place predominantly at N-3.[3,12] 9-Allyladenine has also been prepared from 5-amino-4,6-dichloropyrimidine.[13]

(12) C. J. Abshire and L. Beringuet, *Can. J. Chem.*, **42**, 1599 (1964).

(13) C. Temple, Jr., and C. L. Kussner, unpublished observations.

(14) P. Brookes and P. D. Lawley, *J. Chem. Soc.*, 539 (1960); J. W. Jones and R. K. Robins, *J. Am. Chem. Soc.*, **85**, 193 (1963).