hibiting an identical infrared spectrum. The melting point range and the difficulty in obtaining crystals suggested the product was a mixture of C-3 epimers. This explanation was strengthened by the n.m.r. spectrum, which showed singlets at 48 (18-CH_3) and 122 (six protons, 17β-$OCOCH_3$ and $N{=}NCOCH_3$), a broad singlet at 56 (19-CH_3), a doublet at 115.5 and 117 (equal mixture of 3α- and 3β-$COCOCH_3$), and a multiplet at 266–287 c.p.s. (1 proton, 17β-$C\mathit{H}OCOCH_3$); $\nu_{max}^{CS_2}$ 1760 and 1740 ($OCOCH_3$, $N{=}NCOCH_3$), 1250, and 1225 ($OCOCH_3$); and $\lambda_{max}^{95\%\ EtOH}$ 223 mμ (ε 1560) and 317 mμ (ε 162).

Anal. Calcd. for $C_{25}H_{38}N_2O_5$: C, 67.23; H, 8.58; N, 6.27. Found: C, 67.04; H, 8.57; N, 6.41.

Pyrolysis of VIII.—A solution of VIII (446 mg.) in xylene (45 ml.) was refluxed under a nitrogen atmosphere for 45 min. The solvent was evaporated under reduced pressure, to leave a solid residue of purity greater than 95% as judged by t.l.c. Crystallization of the residue from methanol (30 ml.) at −10° afforded 210 mg. of white crystals: m.p. 120–151° (capillary); $\nu_{max}^{CS_2}$ 1740 ($OCOCH_3$), 1670 ($C{=}CO$), and 1250 cm.$^{-1}$ ($OCOCH_3$). The ultraviolet spectrum showed only end absorption. The n.m.r. spectrum showed singlets at 48 (six protons, 18-CH_3, 19-CH_3), 122, and 124 (two $OCOCH_3$ groups), a doublet (J = 5 c.p.s.) at 85 and 90 ($\mathit{CH}_3\overset{|}{\underset{|}{C}}H$), a quartet ($J$ = 5 c.p.s.) at 370, 375, 380, and 385 ($\mathit{H}\overset{|}{\underset{|}{C}}CH_3$), a multiplet at 275 to 290 (17β-$C\mathit{H}OCOCH_3$), and a broad, one-proton singlet centered at 266 c.p.s. ($OC{=}C\mathit{H}$).

Anal. Calcd. for $C_{25}H_{38}O_5$: C, 71.74; H, 9.15; N, 0.00. Found: C, 71.99; H, 9.17; N, 0.15 ± 0.3.

Hydrolysis of the Pyrolysis Product IX.—A solution of IX (50 mg.) in warm ethanol (10 ml.) was diluted with water (4 ml.) and 3 drops of hydrochloric acid. After standing at room temperature for 1 hr. the solvent was evaporated under reduced pressure. The white, crystalline residue was identified as pure androstan-17β-ol-3-one acetate by t.l.c., infrared, and n.m.r. spectral analysis.

Acknowledgment.—We take pleasure in thanking Dr. M. E. Wall, director of this laboratory, for his encouragement and advice.

Rearrangement. II. Pyrolysis and Acetolysis of Cyclohexanemethyl *p*-Toluenesulfonate

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The pyrolysis of some cyclohexanemethyl derivatives has been investigated by several groups of workers in recent years. Two different mechanisms have been reported: one a *cis* elimination giving exclusively methylenecyclohexane, and the other a carbonium ion type reaction giving isomeric cycloalkenes. The former is patterned after the widely accepted proposal of Hurd and Blunck[3] for carboxylic esters, involving a quasi, six-membered ring as a transition state and adapted in the cyclohexane series for the pyrolysis of cyclohexanemethyl acetate[4] and N,N-dimethylcyclohexanemethylamine oxide.[4,5] The latter involves the pyrolysis of cyclohexanemethyl borate.[6] No comparable experiments have yet been made for the pyrolysis of cyclohexanemethyl *p*-toluenesulfonate (I).[7]

The recrystallized I, when heated to 200° at reduced pressure under nitrogen, readily decomposed. The crude product, collected in a Dry Ice cooled trap, was analyzed by gas chromatography. Each component was separated by preparative-scale gas chromatography and identified by comparison of its n.m.r. spectrum and gas chromatographic relative retention time with those of an authentic sample. The product consisted of 1-methylcyclohexene (56.6%), 3-methylcyclohexene (8.9%), methylenecyclohexane (1.1%), cycloheptene (6.5%), cyclohexene (2%), methylcyclohexane (20.4%), and toluene (4.5%).

Pyrolytic *cis* elimination of I would be expected to give predominantly methylenecyclohexane, as observed in the runs with the above acetate and amine oxide. The analysis, however, revealed only 1.1% of methylenecyclohexane in the products. Rearranged compounds predominated, instead. The fact that 1-methylcyclohexene is thermodynamically more stable than methylenecyclohexane[8] may suggest that the latter, formed initially by *cis* elimination of I, subsequently might have rearranged to the former during reaction. This possibility was excluded by a control experiment showing that isomerization of exocyclic to endocyclic double bonds scarcely occurred under the experimental conditions employed. The possibility that the pyrolysis proceeds through a *cis* elimination mechanism, hence, may be eliminated. Unexpectedly, the saturated compound methylcyclohexane was formed in fairly high yield in contrast to its nonformation as reported in the pyrolysis of the acetate, amine oxide, and borate. The formation of the rearranged–unrearranged cycloalkenes might be explained in terms of either carbonium ions or free radicals, whereas with the formation of the saturated compound carbonium ion disproportionation might be less favorable than radical-pair disproportionation in some respects under the experimental conditions used. Abstraction of a hydride from a carbonium ion would give a carbonium ion with two positive charges. A similar, unfavorable situation would result if a hydride is abstracted from the cyclohexanemethyl group in I, followed by the breaking of the C–O bond. It seems also unlikely to assume hydride abstraction by carbonium ion from the *p*-toluenesulfonate group. There was no diolefinic hydrocarbon found which might be formed by abstraction of a hydride from an olefinic hydrocarbon, followed by loss of a proton. No hydride donor was added to the reaction system, but hydrides might be available from some other decomposed fragments. Further discussion on the mechanism should not be given without further experimental evidence, but it is likely that the pyrolysis might proceed partially, if not predominantly, through pathways other than those reported by previous workers.[4–6] Further experiments are being carried out to elucidate its nature.

Toluene might be formed from cyclohexanemethyl and/or *p*-toluenesulfonate groups. Numerous investi-

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[1] To whom inquiries should be addressed.

[2] Responsible for n.m.r. analysis.

[3] C. D. Hurd and F. H. Blunck, *J. Am. Chem. Soc.*, **60**, 2419 (1938).

[4] H. E. Baumgarten, F. A. Bower, and T. T. Okamoto, *ibid.*, **79**, 3145 (1957).

[5] A. C. Cope, C. L. Bumgardner, and E. E. Schweizer, *ibid.*, **79**, 4729 (1957).

[6] O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26**, 4193 (1961).

[7] J. Blackwell and W. J. Hickinbottom [*J. Chem. Soc.*, 366 (1963)] have reported that isomerization of the cyclohexanemethyl group to 1-methylcyclohexyl occurred during alkylation of the aromatic nuclei by the thermal decomposition of I in toluene and phenol.

[8] (a) R. B. Turner and R. H. Garner, *J. Am. Chem. Soc.*, **79**, 253 (1957); **80**, 1424 (1958); (b) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and Z. Jacura, *ibid.*, **81**, 3153 (1959).

gations on catalytic aromatizations of methylcyclohexane and 1-methylcyclohexene to toluene at high temperatures have been reported, but our reaction temperature was well below those used in such aromatizations. In addition, no catalyst was employed. Toluene was formed also in the acetolysis of I, whereas its formation has been not mentioned in the pyrolysis of the acetate, amine oxide, and borate. Possible intermediate methylcyclohexadienes were not found in the product from I within the limits of detectability by gas chromatography and n.m.r. spectroscopy. The whole reaction mixture collected in a Dry Ice cooled trap had offensive odor characteristic of sulfur oxides, and the water extract of the mixture was acidic. These facts may suggest that the toluene arose from the *p*-toluenesulfonate group.[9]

Mori has reported that the acetolysis[10] of I gave unrearranged cyclohexanemethanol (80% yield, after saponification of the product acetate) and probably methylenecyclohexane (1.4%), and that the acetolysis, based on kinetic studies, is essentially unimolecular involving a carbonium ion. If so, complicated rearrangements would be expected. Reinvestigation of the acetolysis of I showed the product analysis different from Mori's in some respects. The product from I was separated into two fractions by distillation and each fraction was analyzed by gas chromatography. The low-boiling fraction (about 16% yield) was a mixture of 1-methylcyclohexene, 3-methylcyclohexene, methylenecyclohexane, cycloheptene, and toluene in ratios of 92.5:1:1.5:2:3. The high-boiling fraction (about 53% yield) consisted of the acetic esters of 1-methylcyclohexanol, cyclohexanemethanol, and cycloheptanol in ratios of 4:45:1. Trace amounts of these three alcohols as such also were detected. The thermodynamically stable cycloalkene[11] and the unrearranged acetic ester predominated, but considerable amounts of the rearranged acetic esters were also formed. It seems improbable to assume that the acetates of 1-methylcyclohexanol and cycloheptanol, when saponified, yielded cyclohexanemethanol. The possibility of isomerization of cyclohexanemethyl acetate to the above two acetates was excluded by a control experiment which demonstrated that cyclohexanemethyl acetate, when heated at 115° for 50 hr. in glacial acetic acid solution containing sodium acetate and *p*-toluenesulfonic acid, did not isomerize to its isomers. The rearranged alcohols and their acetates may be formed through a carbonium ion type rearrangement. The formation of small amounts of alcohols is probably due to the presence of water in the glacial acetic acid used for the acetolysis. Water is known to be much more nucleophilic than acetic acid.[12] The formation of the rearranged alcohols and their acetates from the corresponding cycloalkenes, however, may not be negligible.[13] In view of the above facts, the most probable conclusion is that the acetolysis proceeds through a direct displacement[14] of the *p*-toluenesulfonate group by solvents as well as through a carbonium ion type rearrangement.

Experimental[15]

Preparation of Alcohols.—1-Methylcyclohexanol, b.p. 68° at 20 mm. (lit.[16] b.p. 55–56° at 10 mm.), cyclohexanemethanol, b.p. 91–92° at 18 mm. (lit.[17] b.p. 88–93° at 18 mm.), and cycloheptanol, b.p. 184–185° (lit.[18] b.p. 184–187°), were prepared by usual procedures from cyclohexanone and methylmagnesium iodide, cyclohexylmagnesium chloride and paraformaldehyde, and cycloheptanone and lithium aluminum hydride, respectively.

Preparation of Acetates.—1-Methylcyclohexyl acetate, b.p. 177° (lit.[19] b.p. 178–179°), cyclohexanemethyl acetate, b.p. 83–85° at 15.5 mm. (lit.[20] b.p. 199–201° at 740 mm.), and cycloheptyl acetate, b.p. 199° (lit.[21] b.p. 199–200.5°), were prepared from the corresponding alcohols and an excess of acetic anhydride in the presence of anhydrous sodium acetate.

Dehydration of 1-methylcyclohexanol and cycloheptanol was effected according to the directions of Traynelis, *et al.*[22] The former gave an olefin mixture, b.p. 107–110°. Each component was separated by preparative-scale gas chromatography. The separated 1-methylcyclohexene boiled at 110°, and the methylenecyclohexane at 102° (lit.[8a] b.p. 110.2 and 102.5°, respectively). The latter gave cycloheptene, b.p. 114.5–115° (lit.[23] b.p. 115°).

3-Methylcyclohexene.—A mixture of *cis*- and *trans*-3-methylcyclohexanol was dehydrated following the method of Mosher,[16] yielding an olefin mixture. Gas chromatographic analysis showed it to consist of at least four components. The component corresponding to 3-methylcyclohexene was separated by gas chromatography, b.p. 103° (lit.[24] b.p. 104°).

Pyrolysis of Cyclohexanemethyl *p*-Toluenesulfonate.—The *p*-toluenesulfonate was prepared from cyclohexanemethanol (34.2 g., 0.3 mole) and *p*-toluenesulfonyl chloride (57.2 g., 0.3 mole) in anhydrous pyridine. The crude product was recrystallized from a mixture of petroleum ether (b.p. 30–50°) and methanol to give white needles in 65% yield (52.5 g.), m.p. 32–33° (lit.[10b] m.p. 32–33°).

Pyrolysis was conducted in a 100-ml., round-bottomed flask equipped with a side arm for introduction of nitrogen. The flask was connected to a 40-cm. Vigreux-type distilling column, which was connected in turn to a trap immersed in a Dry Ice–methanol bath, and a vacuum pump. The flask was charged with the *p*-toluenesulfonate (13.4 g., 0.05 mole), evacuated to 2 mm., and immersed in an oil bath. The bath was heated rapidly to 200°. After a few minutes, the sulfonic ester began to decompose, and the decomposition continued for about 1 min. The product in the trap was taken up with ether, washed with dilute sodium hydroxide solution and water, and dried over anhydrous magnesium sulfate, and the ether was removed, leaving a hydrocarbon mixture weighing between 3.2–3.6 g. The hydrocarbon mixture was submitted to gas chromatographic and n.m.r. analyses.

The hydrocarbons collected in 10 sec. after the decomposition began still indicated essentially the same hydrocarbon compo-

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[9] This conclusion may be supported by the fact that the pyrolysis of cyclohexanemethyl methanesulfonate also yielded cycloalkenes and methylcyclohexane, but no toluene: unpublished results.

[10] (a) N. Mori, *Bull. Chem. Soc. Japan*, **35**, 1755 (1962); (b) C. F. Wilcox, Jr., and S. S. Chibber [*J. Org. Chem.*, **27**, 2332 (1962)] also have investigated the solvolysis of I, but their approach has been directed exclusively toward kinetic studies.

[11] Even if the exocyclic olefin were formed in high yield, the olefin would predominantly isomerize to the more stable *endo* isomer under the experimental conditions employed, which are very favorable for the exo–endocyclic olefin isomerization. See ref. 8.

[12] C. G. Swain, R. B. Mosely, and D. E. Bown, *J. Am. Chem. Soc.*, **77**, 3731 (1955).

[13] Cope, *et al.*, have reported that the products from the equilibrations of the five-, six-, and seven-membered cycloalkenes contained the corresponding 1-methylcycloalkanols and their acetates. See ref. 8b.

[14] It is unreasonable to assume that the unrearranged acetate (90% of the product acetates) arose predominantly from the cyclohexanemethyl carbonium ion, since the unstable primary carbonium ion would mainly rearrange to the more stable tertiary or secondary carbonium ions before solvent attack or loss of a proton.

[15] All melting points and boiling points are uncorrected.

[16] W. A. Mosher, *J. Am. Chem. Soc.*, **62**, 552 (1940).

[17] H. Gilman and W. E. Catlin, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, p. 188.

[18] D. N. Matthews and E. I. Becker, *J. Org. Chem.*, **21**, 1317 (1956).

[19] J. G. Traynham and O. S. Pascual, *ibid.*, **21**, 1362 (1956).

[20] A. Fawarsky and I. Borgmann, *Ber.*, **40**, 4865 (1907).

[21] N. A. Nelson, J. H. Fassnacht, and J. U. Piper, *J. Am. Chem. Soc.*, **83**, 206 (1961).

[22] V. J. Traynelis, W. L. Hergenrother, H. T. Hanson, and J. A. Valicenti, *J. Org. Chem.*, **29**, 123 (1964).

[23] R. Willstätter, *Ann.*, **317**, 221 (1901).

[24] N. D. Zelinsky, *Ber.*, **57**, 2055 (1924).

sition to that obtained at the end of the pyrolysis. Considerable amounts of tar-like substances remained in the reaction flask after the pyrolysis of the *p*-toluenesulfonate, but no attempt was made to identify the residue.

Acetolysis of cyclohexanemethyl *p*-toluenesulfonate was reinvestigated with some modifications (in an open system at 115° for 50 hr., instead of in a sealed ampoule at 110° for 60 hr.). In a 500-ml., round-bottomed flask equipped with a reflux condenser, the top of which was connected to a trap immersed in Dry Ice–methanol bath, there were placed the *p*-toluenesulfonate (26.8 g., 0.1 mole), anhydrous sodium acetate (9 g., 0.11 mole), and glacial acetic acid (250 ml.). The flask was heated for 50 hr. in an oil bath at 115°, then was cooled to 0–5°. The contents was neutralized with dilute sodium hydroxide solution and extracted with ether. The trap and condenser were rinsed with ether. The combined ether extracts were dried over magnesium sulfate, and distilled, giving 1.5 g. of a low-boiling fraction (b.p. 90–112°), and 8.8 g. of a high-boiling fraction [55° (20 mm.) to 85° (15 mm.)]. No attempt was made to identify the residue.

Product Analysis.—Gas chromatographic analysis was carried out using 500 × 0.35 cm. columns packed with 80–100-mesh Celite which was coated with the appropriate stationary phase. The stationary phases employed were (A) 30% (w./w.) of a 40% solution of silver nitrate in tetraethylene glycol; (B) 25% (w./w.) of octyl phthalate; and (C) 30% (w./w.) of Apiezon grease L. Columns A and B were used to analyze hydrocarbons at 60 and 100°, respectively. Alcohols and their acetates were analyzed using column C at 150°. Helium outlet flow rates were 45 (A), 55 (B), and 60 (C) cc./min. The relative retention time is the ratio of a retention time of a substance to the retention time of benzene as measured from an air peak. Quantitative analysis was done following the procedure of Messner, *et al.*,[25] using benzene as an internal standard.

The n.m.r. spectra were determined at 25° in carbon tetrachloride on a Varian Associates Model V-4311 high-resolution spectrometer operating at 60 Mc. with tetramethylsilane (τ 10.00) as an internal standard. The resonance lines used for structural assignment follow: 1-methylcyclohexene (an incompletely resolved multiplet, τ 4.71, an olefinic proton; an incompletely resolved doublet, 8.40, methyl protons), 3-methylcyclohexene (a complex multiplet, three main lines, τ 4.44, 4.47, and 4.53, olefinic protons; an asymmetrical doublet, 9.00 and 9.11, apparent coupling constant J = 6.6 c.p.s., methyl protons), methylenecyclohexane (an incompletely resolved quintet, τ 5.47, terminal methylene protons), cycloheptene (a triplet, τ 4.30, J = 3.7 c.p.s., olefinic protons), cyclohexene (a triplet, τ 4.43, J = 1.5 c.p.s., olefinic protons), methylcyclohexane (an asymmetrical doublet, τ 9.07 and 9.15, J = 4.8 c.p.s., methyl protons), and toluene (a singlet, τ 2.90, ring protons; a singlet, 7.66, methyl protons).

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[25] A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

The Reaction of Benzyne with Phenyl Isocyanate

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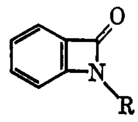
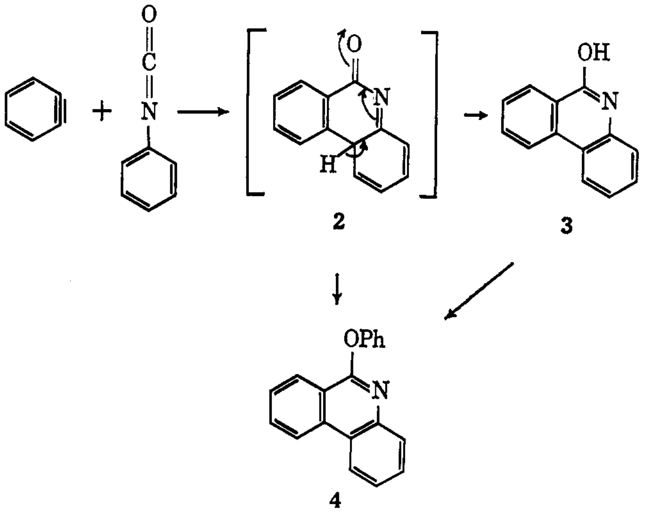
Consideration of the chemistry of benzyne[2] and especially reactions in which benzyne has undergone cyclic addition with an olefin[3] suggested that benzazetidinones[4] (1) might be produced by the reaction of benzyne with isocyanates.[5]



1

However, when diazotized anthranilic acid[6] was decomposed thermally in benzene in the presence of excess phenyl isocyanate, no product with properties attributable to 1 (R = Ph) was isolated. Chromatography of the complex reaction mixture on Florisil resulted in the isolation of phenanthridinone[7] (3) and 9-phenoxyphenanthridine[8] (4) in low yields. The formation of 3 and 4 is most simply formulated as involving an initially formed Diels–Alder adduct (2).[9] A proton shift restores aromaticity to the system to produce phenanthridinone (3). Reaction of 3 with a second molecule of benzyne accounts for the formation of 9-phenoxyphenanthridine (4). Alternately, reaction of benzyne with the Diels–Alder adduct 2 would produce 4 directly.



Phenyl isocyanate dimer,[10] 1,3,5-triphenylbiuret,[11] and several fractions containing highly colored, heterogeneous, polar material were isolated. Structure elucidation of this material was not undertaken.

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[1] National Institutes of Health Predoctoral Fellow, 1962–1964.

[2] See H. Heaney, *Chem. Rev.*, **62**, 81 (1962); J. F. Bunnett, *J. Chem. Educ.*, **38**, 278 (1961); R. Huisgen in "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp. 36–87.

[3] See, for example, H. E. Simmons, *J. Am. Chem. Soc.*, **83**, 1657 (1961); M. E. Kuehne, *ibid.*, **84**, 837 (1962).

[4] A number of benzazetidinone structures have been assigned in the early literature; however, modern reviewers have either ignored these reports altogether or viewed them with skepticism: A. H. Cook, *Quart. Rev.* (London), **2**, 243 (1948); H. T. Clark, J. R. Johnson, and R. Robinson, "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949, pp. 983–984.

[5] Recently isocyanates have been shown to undergo similar ring closures with enamines to form azetidinones: M. Perelman and S. A. Mizsak, *J. Am. Chem. Soc.*, **84**, 4988 (1962); G. Opitz and J. Koch, *Angew. Chem.*, **75**, 167 (1963).

[6] M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).

[7] P. A. S. Smith, *ibid.*, **76**, 431 (1954).

[8] D. H. Hey and T. M. Moynehan, *J. Chem. Soc.*, 1563 (1959).

[9] J. Nieuwenhuis and J. F. Arens [*Rec. trav. chim.*, **76**, 999 (1957)] formulated the reaction of phenyl isocyanate with ethoxyacetylene similarly.

[10] I. C. Kogon, *J. Am. Chem. Soc.*, **78**, 4911 (1956).

[11] I. C. Kogon, *ibid.*, **79**, 2253 (1957).