nesium sulfate. The methylene chloride was removed at the water-pump without heating. The infrared spectrum of the blue liquid obtained was that of 2-nitroso-2-benzoyloxypropane. No trace of the aromatic nitro absorption of VIIIc was evident.

1-Nitroso-1-benzoyloxycyclohexane (VIIId). (A).—Sodium cyclohexanenitronate (20 g., 0.132 mole) was suspended in 200 ml. of dry methylene chloride and the mixture was cooled in an ice–salt-bath. Benzoyl chloride (16 g., 0.111 mole) dissolved in 50 ml. of methylene chloride was added to the stirred suspension during 0.5 hour. Stirring was continued for an additional three hours at −10°. The green reaction mixture was washed with water, with 5% sodium hydroxide and with water again, and then dried over anhydrous potassium carbonate. The solvent was removed at the water pump without heating to yield 20.8 g. of a green oil (0.076 mole, 68% based on benzoyl chloride). No solid material was deposited when the green oil was stored in the deep freeze. The infrared spectrum in methylene chloride had bands at 5.80 (ester carbonyl) and 6.39 μ (aliphatic monomeric nitroso). During short path distillation (0.25 mm., bath temperature 70°) extensive decomposition occurred, but a small amount of a mobile bright blue oil was obtained, $n^{26}\text{D}$ 1.5250, $\lambda_{\max}$ 667 (ϵ 23.8) in CH_2Cl_2.

Anal. Calcd. for $C_{13}H_{15}O_3N$: C, 66.93; H, 6.48; N, 6.01. Found: C, 66.88; H, 6.64; N, 5.78.

(B) **Method of Iffland and Criner.**[12]—Lead tetrabenzoate[21] (25 g., 0.036 mole) was suspended in 100 ml. of methylene chloride and the mixture was cooled in an ice-bath. Cyclohexanone oxime (3.68 g., 0.033 mole) was added in small portions to the stirred suspension over a period of 45 minutes. Stirring was continued for 15 minutes and then 10 ml. of water was added to the green suspension. Stirring was continued for an additional ten minutes, during which time the green reaction mixture turned blue and a white precipitate was washed with 25 ml. of methylene chloride. The filtrate and washes were combined and washed with 25-ml. portions of a 5% sodium bicarbonate solution (until the aqueous phase remained basic to litmus) and then with 25 ml. of water. The bright blue solution was dried over anhydrous potassium carbonate. The solvent was removed at the water-pump without heating to give 6.6 g. (0.028 mole, 86% based on cyclohexanone oxime) of a bright blue liquid. Its infrared spectrum was identical in every respect with that obtained by method A.

α-Phenylnitroethane. Modification of the Method of Kornblum.[24]—α-Phenylethyl bromide (111 g., 0.595 mole) was added to a solution of urea (80 g., 1.33 moles), phloroglucinol (80 g., 0.64 moles) and sodium nitrite (72 g., 1.04 moles) in 1.2 l. of dimethylformamide. The reaction mixture was stirred at room temperature for 45 hours and then poured into 3 l. of ice-water. The water solution was extracted with five 200-ml. portions of pentane. The extracts were combined, washed with five 150-ml. portions of water and dried over anhydrous magnesium sulfate. Evaporation of the pentane gave 32 g. of a red liquid, the infrared spectrum of which showed the presence of a considerable amount of a carbonyl containing material (5.90 μ). To remove the carbonyl impurity, a Girard[25] separation was employed. The non-ketonic fraction from the Girard separation was distilled through a Vigreux column. The following fractions were obtained (colorless liquids):

Fraction	Wt., g.	B.p. °C.	B.p. Mm.	$n^{25}\text{D}$
1	4.95	68–78	0.65	1.5189
2	11.1	78-80	.65	1.5202
3	8.06	80	.65	1.5208

α-Phenylnitroethane has reported boiling points of 92° (2 mm.)[26] and 135° (25 mm.).[27] The literature values for the index of refraction are: $n^{20}\text{D}$ 1.5215[31] and $n^{25}\text{D}$ 1.5212.[27]

Fraction 1 was contaminated with carbonyl-containing substances as shown by the infrared spectrum (5.90 μ). Fraction 2 and 3 weighed 19.16 g. (0.127 mole, 21%). The infrared spectrum showed: $\lambda_{\max}^{CHCl_3}$ 6.45 μ (aliphatic nitro), no peak was observed at 5.90 μ.

Benzoylation of Sodium α-Phenylethanenitronate.—Benzoyl chloride and sodium α-phenylethanenitronate were allowed to react at −80° as previously described for compound VIIa. The low temperature infrared spectrum of VIIb in methylene chloride had bands at 5.68 and 6.21 μ. Upon warming to room temperature, the spectrum changed to that of 1,1,1-benzoyloxynitrosophenylethane (VIIIb) with bands at 5.77 and 6.36 μ. In addition, a band appeared at 5.94 μ (probably acetophenone).

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[24] N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto and G. E. Graham, THIS JOURNAL, **78**, 1497 (1956).

(25) A. Girard and G. Sandulesco, *Helv. Chim. Acta*, **19**, 1095 (1936).

(26) N. Kornblum, L. Fishbein and R. A. Smiley, THIS JOURNAL, **77**, 6265 (1955).

(27) M. Konowalow, *Ber.*, **27**, ref., 193 (1894).

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[CONTRIBUTION FROM BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

Many-membered Carbon Rings. XVI. Acetolysis of 5,5-Dimethylcyclononanol Tosylate[1,2]

BY A. T. BLOMQUIST AND YVONNE C. MEINWALD

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Acetolysis of 5,5-dimethylcyclononanol tosylate has been studied with the objective of ascertaining the role of annular methyl groups in medium size ring reactions. The rate of acetolysis at 35° was about half that observed for cyclononyl tosylate. Analysis of the acetolysis products indicated that transannular migration of methyl groups occurs to the extent of less than 5%, if at all.

Although a number of transannular hydride migrations have been observed in reactions of medium size rings,[3] there have been no reported instances of shifts of alkyl or aryl groups across such rings. It was of interest, therefore, to seek evidence for such phenomena. The first effort to discern the role of annular alkyl groups in medium size ring reactions has been a study of the acetolysis of 5,5-dimethylcyclononanol tosylate (I) under Winstein's "limiting conditions."[4] Some of the possible transformations that might be expected to occur in the acetolysis of I are indicated in the dia-

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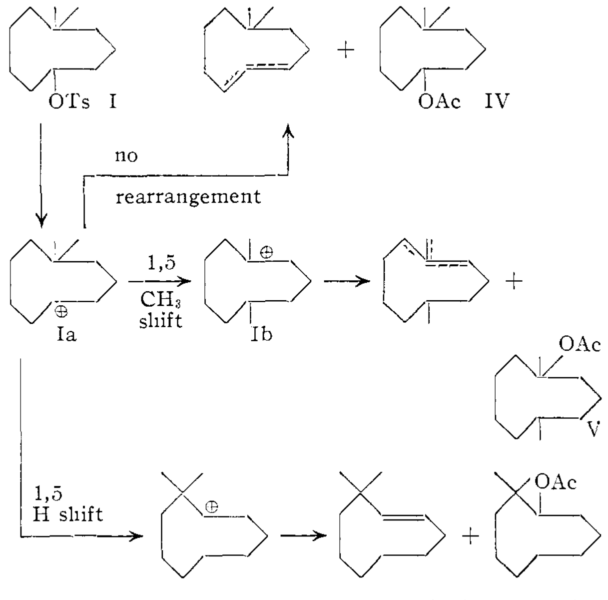
(1) This study was supported by the National Science Foundation, Grant NSF-G2922.

(2) For the preceding paper in this series see A. T. Blomquist and Y. C. Meinwald, *J. Org. Chem.*, **22**, in press (1957).

(3) (a) V. Prelog, H. J. Urech, A. A. Bothner-By and J. Würsch, *Helv. Chim. Acta*, **38**, 1095 (1955); (b) H. J. Urech and V. Prelog, *ibid.*, **40**, 477 (1957); (c) V. Prelog and M. Speck, *ibid.*, **38**, 1786 (1955); (d) A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5881 (1952); (e) V. Prelog and W. Küng, *Helv. Chim. Acta*, **39**, 1394 (1956).

(4) S. Winstein, C. Hanson and E. Grunwald, THIS JOURNAL, **70**, 812 (1948).

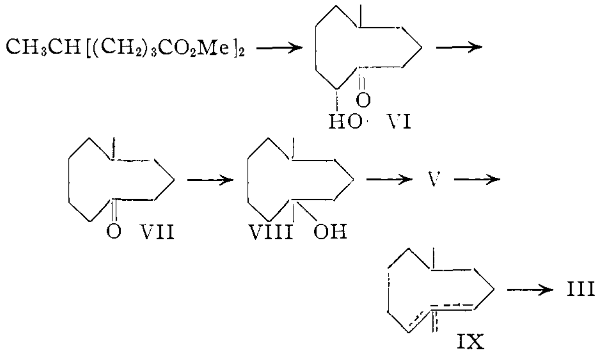
gram. On the basis of the scanty data available, a methyl group in I might be in a position favorable for migration, with the driving force being the formation of a tertiary carbonium ion such as Ib.



Comparison of the rate of acetolysis of I with that observed for the unsubstituted homolog, cyclononyl tosylate,[5] would provide information about the possible participation of the annular methyl groups in the rate-determining step, while analysis of the products of the acetolysis would indicate the extent to which methyl migration had occurred subsequent to the rate-determining ionization step. Product study could be simplified by reducing all olefinic components to saturated hydrocarbons and then comparing with authentic specimens of 1,1- and 1,5-dimethylcyclononane (II and III, respectively).

Compound I was obtained easily by treatment of the previously described 5,5-dimethylcyclononanol[6] with *p*-toluenesulfonyl chloride. The authentic hydrocarbon II was prepared as described previously,[6] while the acetate IV was prepared from the corresponding alcohol in the usual way. Authentic specimens of III and V, possible products of rearrangement, were synthesized as described below.

Dimethyl δ-methyleneazelate, obtained from isobutylene and acrylic ester,[7] was reduced to dimethyl δ-methylazelate. Cyclization of the latter with sodium in an anhydrous xylene–toluene mixture afforded the expected acyloin VI in 60% yield. The cyclic ketone VII was obtained in 60% yield by reduction of VI with zinc and hydrochloric acid in acetic acid. Addition of methylmagnesium iodide to VII gave the tertiary alcohol VIII (90% yield) which was converted to the desired tertiary acetate V by acetylation with ketene. Pyrolysis of V at 450° afforded a mixture of olefins separable



by distillation into cyclic and acyclic fractions.[8] The cyclic olefin fraction, indicated by infrared analysis as comprising largely the exomethylenic isomer, was reduced to the desired hydrocarbon III by catalytic hydrogenation.

It is considered likely that the authentic V and III were mixtures of *cis* and *trans* isomers since the synthetic methods used were not stereospecific. The correctness of this view is indicated by the wide melting range of the synthetic VIII. Since any rearrangement accompanying solvolysis might also be non-stereospecific, no difficulty was anticipated on this account. The final observation that both the elimination and substitution products were essentially indistinguishable from the authentic unrearranged products reduces the importance of characterizing the individual stereoisomers of the possible rearranged products.

The rate of acetolysis of I and of cyclononyl tosylate were measured at 35° in anhydrous acetic acid containing excess acetic anhydride (see Table I). The rate constant for the unsubstituted tosylate was in excellent agreement with that reported by Brown and co-workers.[5] The results indicated clearly that there is no transannular participation of the methyl group in the initial ionization step.

TABLE I

ACETOLYSIS OF CYCLONONYL TOSYLATES

Tosylate	Rate constant k_1, sec.$^{-1}$ $\times 10^5$	Products, % Olefin	Acetate
Cyclononyl	8.75 8.72 (ref. 5)	35	43
5,5-Dimethylcyclononyl	4.70	46	50

Infrared analysis of the olefinic fractions indicated that they comprised mainly *cis*-olefins. Infrared examination of the acetate fraction and the reduced olefin fraction from the acetolysis of I indicated that they were identical with pure authentic IV and II, respectively. Since the infrared analysis of known mixtures of authentic IV and V as well as II and III was sensitive to *ca.* ±5% it can be concluded that methyl migration in the acetolysis of I, if it occurred at all, did so to the extent of less than 5%.[9]

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(5) H. C. Brown and J. Ham, THIS JOURNAL, **78**, 2735 (1956); V. Prelog and R. Heck, *Helv. Chim. Acta*, **38**, 1541 (1955).

(6) A. T. Blomquist, E. S. Wheeler and Y. Chu, THIS JOURNAL, **77**, 6307 (1955).

(7) C. J. Albisetti, N. G. Fisher, M. J. Hogsed and R. M. Joyce, *ibid.*, **78**, 2637 (1956).

(8) The acyclic fraction was probably a mixture of the dienes $CH_2=CHCH(CH_3)CH_2CH_2CH(CH_3)CH=CH_2$ and $CH_2=C(CH_3)CH_2CH_2CH_2CH_2CH(CH_3)CH=CH_2$; see A. T. Blomquist and P. R. Taussig, *ibid.*, **79**, 3505 (1957). Its composition was not investigated in detail in the course of this work.

(9) The technique of vapor-phase chromatography was not useful in the product study made here. Although a number of columns were tried, it was not possible to resolve mixtures of the pure hydrocarbons II and III. The columns used comprised dinonyl phthalate, silicone oil, tri-tolyl phosphate and diglycerol on various supports.

Experimental Part

Cyclononyl tosylate was prepared as described by Brown,[5] m.p. 43–44°.

5,5-Dimethylcyclononyl tosylate (I) prepared as described above, was obtained as a viscous liquid; sapn. equiv.: calcd. 324.5, found 326.

Kinetic Measurements.—The solvent used was prepared as described by Brown, *et al.*,[5] while the procedure followed for determining rate constants was that of Winstein and coworkers.[4]

Product Separation and Identification. A. Cyclononyl Tosylate.—Acetolysis of 2.96 g. (0.01 mole) of cyclononyl tosylate in 20 ml. of anhydrous acetic acid was carried out in a constant temperature bath at 35°. After the reaction was completed, the mixture was poured into 20 ml. of 10% aqueous sodium carbonate solution and extracted with ether. The ether extract was washed with dilute sodium carbonate solution and water, dried over magnesium sulfate and then evaporated. The residue (1.5 g.) was chromatographed on alumina and eluted with pentane to give 0.43 g. (35%) of *cis*-cyclononene, $n^{22}\text{D}$ 1.4786, and 0.90 g. (43%) of cyclononyl acetate, $n^{22}\text{D}$ 1.4643. The infrared spectra of the two products were identical with those of authentic *cis*-cyclononene and cyclononyl acetate.

B. **5,5-Dimethylcyclononyl Tosylate (I).**—The acetolysis products from 3.24 g. (0.01 mole) of I were isolated as described in part A above. After chromatography there was obtained 0.7 g. (46%) of olefinic products, $n^{25}\text{D}$ 1.4743, and 1.05 g. (50%) of the acetate IV, $n^{25}\text{D}$ 1.4612. The infrared spectrum of this acetate was identical with that of authentic IV described below.

The olefinic product (0.4141 g.) was hydrogenated at 23.7° and 731 mm. over prereduced Adams catalyst in glacial acetic acid. It absorbed 70.0 ml. (100.9% of one molar equivalent) of hydrogen. The usual work-up of the hydrogenated product gave, after a final flash distillation, 0.38 g. of colorless liquid II, $n^{25}\text{D}$ 1.4600. Authentic II, $n^{25}\text{D}$ 1.4604, b.p. 104° (36 mm.), was prepared as described previously.[6] The infrared spectra of the two samples of II were identical. Both showed the same characteristic absorption at 7.23 and 7.33 μ.

5,5-Dimethylcyclononyl Acetate (IV).—5,5-Dimethylcyclononanol (1 g.) was treated with 2 ml. of acetic anhydride and 4 ml. of pyridine at room temperature for two days. The usual work-up gave 1.1 g. of colorless liquid IV, b.p. 72° (0.3 mm.), $n^{25}\text{D}$ 1.4610, infrared $\lambda_{\max}$ 5.77, 7.24, 7.33 and 8.03 μ.

Anal. Calcd. for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.48; H, 11.29.

Dimethyl δ-methyleneazelate[7] was obtained directly by reaction of two moles of methyl acrylate with one mole of isobutylene at 240° for 28 hr. The ester showed b.p. 124–125° (2.5 mm.) and $n^{25}\text{D}$ 1.4510.

Dimethyl δ-Methylazelate.[7]—Dimethyl δ-methyleneazelate (69 g., 0.3 mole) was hydrogenated in 95% ethanol with Adams catalyst. After the usual work-up, there was obtained 67.5 g. (97%) of the saturated ester having b.p. 108.5–110.5° (1 mm.) and $n^{25}\text{D}$ 1.4378.

Cyclization of Dimethyl δ-Methylazelate.—The acyloin cyclization was carried out in the usual way.[6] The diester (67.5 g., 0.293 mole), diluted with 140 ml. of xylene, was added over a 7.5-hr. period to a stirred refluxing mixture of 2 l. of xylene and 400 ml. of toluene containing 35 g. (1.5 moles) of finely divided sodium. After the usual work-up there was obtained 29.8 g. (60%) of cyclic acyloin VI containing some diketone; b.p. 75–76° (0.5 mm.). The infrared spectrum of this product showed absorption at 2.90 and 5.86 μ.

5-Methylcyclononanone (VII).—The crude VI obtained above (29.8 g., 0.175 mole) was reduced with 90–95% zinc dust as described for the reduction of azeloin to cyclononanone.[10] The crude product was fractionated through an 83-in. Podbielniak column to give 16.7 g. (61%) of the pure ketone VII, b.p. 99° (10 mm.), $n^{25}\text{D}$ 1.4714.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 78.11; H, 11.79.

The semicarbazone derivative of VII showed m.p. 167–168°.

Anal. Calcd. for $C_{11}H_{21}ON_3$: C, 62.52; H, 10.02; N, 19.89. Found: C, 62.75; H, 10.01; N, 20.10.

1,5-Dimethylcyclononanol (VIII).—A solution of 3.02 g. (0.02 mole) of VII in 20 ml. of anhydrous ether was added slowly with stirring to 100 ml. of anhydrous ether containing 0.04 mole of methylmagnesium iodide (from 5.68 g. of methyl iodide and 1 g. of magnesium). After addition was complete, the mixture was refluxed 2 hr. The cooled reaction mixture was poured into 300 ml. of a saturated ammonium chloride solution at 0° and extracted with ether. The ether extract was washed with saturated sodium chloride solution, dried and evaporated. Distillation of the residue gave 3 g. (90%) of viscous liquid VIII, b.p. 78–80° (1.2–1.3 mm.) and $n^{25}\text{D}$ 1.4763, which solidified to soft needles on standing, m.p. 35–48°.

Anal. Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.56; H, 12.82.

1,5-Dimethylcyclononyl Acetate (V).—Ketene was bubbled into a solution of 2.79 g. (0.015 mole) of VIII in 10 ml. of anhydrous ether containing a crystal of *p*-toluenesulfonic acid for 1.5 hr. The reaction mixture was cooled occasionally during this time with an ice–water-bath. The infrared absorption spectrum of the crude reaction mixture showed no hydroxyl absorption at the end of this period. The reaction mixture was washed with dilute sodium carbonate and water, dried and evaporated. Distillation of the crude product gave 3 g. (94%) of the acetate V, b.p. 62° (0.2 mm.), $n^{25}\text{D}$ 1.4607. The infrared spectrum of V showed absorption at 5.78, 7.32 and 8.00 μ.

Anal. Calcd. for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.74; H, 11.12.

Pyrolysis of V.—The acetate V (8.0 g.) was dropped slowly, one drop every 10 sec., under a nitrogen atmosphere into a vertically arranged 16-in. Pyrex tube packed with Carborundum chips and heated at 445–450°. The pyrolysate, collected in a receiver cooled with Dry Ice, was diluted with pentane, washed with water, 10% sodium carbonate solution and finally with water. Distillation of the dried pentane solution through an 83-in. Podbielniak column gave two principal fractions: (a) 1.5 g., b.p. 175–180°, $n^{25}\text{D}$ 1.4400, infrared $\lambda_{\max}$ 11.00 and 11.28 μ; (b) 3.68 g., b.p. 200–202°, $n^{25}\text{D}$ 1.4731, infrared $\lambda_{\max}$ 11.30 μ. Fraction b was redistilled to give IX, b.p. 122–123° (55 mm.), $n^{25}\text{D}$ 1.4738.

Anal. Calcd. for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 87.09; H, 13.05.

1,5-Dimethylcyclononane (III).—The olefinic mixture IX (2.0077 g.) was hydrogenated in acetic acid with prereduced Adams catalyst. The uptake of hydrogen was 353 ml. at 24° and 736.5 mm., corresponding to one mole equivalent of hydrogen. The usual work-up of the mixture after hydrogenation gave 1.8 g. of III, b.p. 118° (50 mm.), $n^{25}\text{D}$ 1.4586, infrared $\lambda_{\max}$ 7.26 μ.

Anal. Calcd. for $C_{11}H_{22}$: C, 85.63; H, 14.37. Found: C, 85.76; H, 14.31.

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(10) A. T. Blomquist, L. H. Liu and J. C. Bohrer, THIS JOURNAL, **74**, 3643 (1952).