The Beckmann Rearrangement and Fragmentation of Substituted Bicyclo[2.2.2]octan-2-one Oximes[1]

KEN-ICHI MORITA AND ZENNOSUKE SUZUKI

The Basic Research Laboratories, Toyo Rayon Company, Ltd., Kamakura, Japan

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The Beckmann rearrangement of variously substituted bicyclo[2.2.2]octan-2-one oximes has been carried out. Effects of substituents on the rearrangement was found to reflect in the ratio of lactam formation to fragmentation. The ratio decreases with substituents in the 1-position in the sequence, H > CH_3 > phenyl, and increases with methyl substituents in the bicyclo[2.2.2]octane ring. The former was ascribed to the electronic effect, and the latter to the steric effect.

The formation of 2-azabicyclo[3.2.2]nonan-3-one (**7**) by Beckmann rearrangement of the oxime of bicyclo[2.2.2]octan-2-one has been reported.[3] The present article describes the Beckmann rearrangement of oximes of variously substituted bicyclo[2.2.2]octan-2-ones[2,4] and the effects of substituents on the ratio of lactam formation to fragmentation.[5]

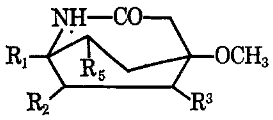
The rearrangement was carried out by the addition of benzenesulfonyl chloride to a suspension or a solution of the oximes in concentrated alkali[3,7] or by the addition of *p*-toluenesulfonyl chloride to a pyridine solution of oximes.[8] In Chart I are summarized the results of the rearrangement of oximes of substituted bicyclo[2.2.2]octan-2-ones, and Table I lists physical constants of the resulting lactams.

All oximes and lactams described in this paper appear to possess only one isomeric form based on physical properties such as n.m.r. spectra. The hydroxyl groups of oximino moieties of oximes **2**–**6** were each shown to possess the *anti* configuration to the bridgehead, based on the evidence of e.s.r. spectra of iminoxy radicals derived from the corresponding oximes.[9] If one assumes that there were no *syn–anti* isomerizations during the Beckmann rearrangement experiments, the lactams should possess the 2-azabicyclo[3.2.2]nonan-3-one structure, since the rearrangements are known to occur stereospecifically with *anti* migration.[10,11]

Structure proofs of lactams were obtained by a combination of physical and chemical methods. N.m.r. spectra of lactams confirmed the existence of an isolated methylene group α to an amide carbonyl, τ 7.25–7.48, and a methoxyl group, τ 6.79–6.87. Infrared spectra are also consistent with the assigned structure. Bands for lactam carbonyls, 1647–1655 cm.$^{-1}$, and for methoxyl groups, 1080–1100 cm.$^{-1}$, were found. The lactam derived from 4-methoxybicyclo[2.2.2]octan-2-one oxime (**2**) lost 1 mole of methanol on acid hydrolysis and afforded 4-aminocyclohexylideneacetic acid (**17**), m.p. 285° dec.

TABLE I

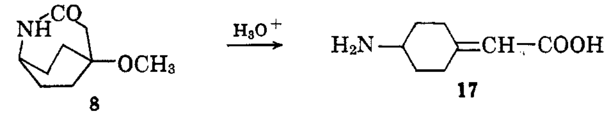
PHYSICAL CONSTANTS OF 2-AZABICYCLO[3.2.2]NONAN-3-ONES

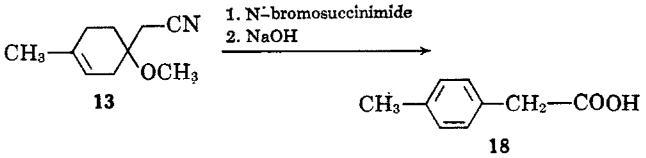


Compd.	Substituents R₁	R₂	R₃	R₅	M.p., °C.	Infrared, $\nu_{C=O}$, cm.$^{-1}$	N.m.r., τ OCH₃	Methylene α to C=O	Bridgehead methyl	Formula	Calcd., % C	H	N	Found, % C	H	N
8	H	H	H	H	94.5–95.0	1647	6.81	7.25	...	$C_9H_{15}NO_2$	63.88	8.94	8.28	63.93	8.92	8.40
9	CH_3	H	H	H	149.5–150.0	1655	6.79	7.22	8.80	$C_{10}H_{17}NO_2$	65.54	9.35	7.64	65.51	9.34	7.60
10	CH_3	H	CH_3	H	108.5–109.0	1653	6.87[a]	7.48[a]	8.82[a]	$C_{11}H_{19}NO_2$	66.97	9.71	7.10	66.85	9.62	7.24
11	CH_3	CH_3	CH_3	CH_3	158.5–159.0	1651	6.81	7.22	8.90	$C_{13}H_{23}NO_2$	69.29	10.29	6.22	69.37	10.33	6.35

[a] In carbon tetrachloride.

The assignment of structures for the nitriles is based on infrared spectra. Bands for nitriles were found at 2250–2270 cm.$^{-1}$ and for methoxyl at 1090–1100 cm.$^{-1}$ Further structure proof was carried out on the nitrile **13** derived from 4-methoxy-1-methylbicyclo[2.2.2]octan-2-one oxime (**3**). Treatment of a carbon tetra-





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[1] Bridged Ring Compounds. V. For part IV, see ref. 2.

[2] K. Morita and T. Kobayashi, *J. Org. Chem.*, **31**, 229 (1966).

[3] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1209 (1960).

[4] K. Morita, M. Nishimura, and Z. Suzuki, *J. Org. Chem.*, **30**, 533 (1965).

[5] A large number of examples has accumulated in which an oxime fragments instead of rearranges to the usual lactam. Notable among compounds undergoing this anomalous reaction are the oximes of bicyclic ketones having bridgeheads[6a] or tertiary carbon atoms[6b,c] adjacent to the oximino functions.

[6] (a) R. W. Cottingham, *J. Org. Chem.*, **25**, 1473 (1960), and literature cited therein; (b) R. K. Hill and R. T. Conley, *J. Am. Chem. Soc.*, **82**, 645 (1960); (c) R. Lukes and J. H. Hofman, *Collection Czech. Chem. Commun.*, **26**, 523 (1961).

[7] M. Gates and S. P. Malchick, *J. Am. Chem. Soc.*, **79**, 5546 (1957).

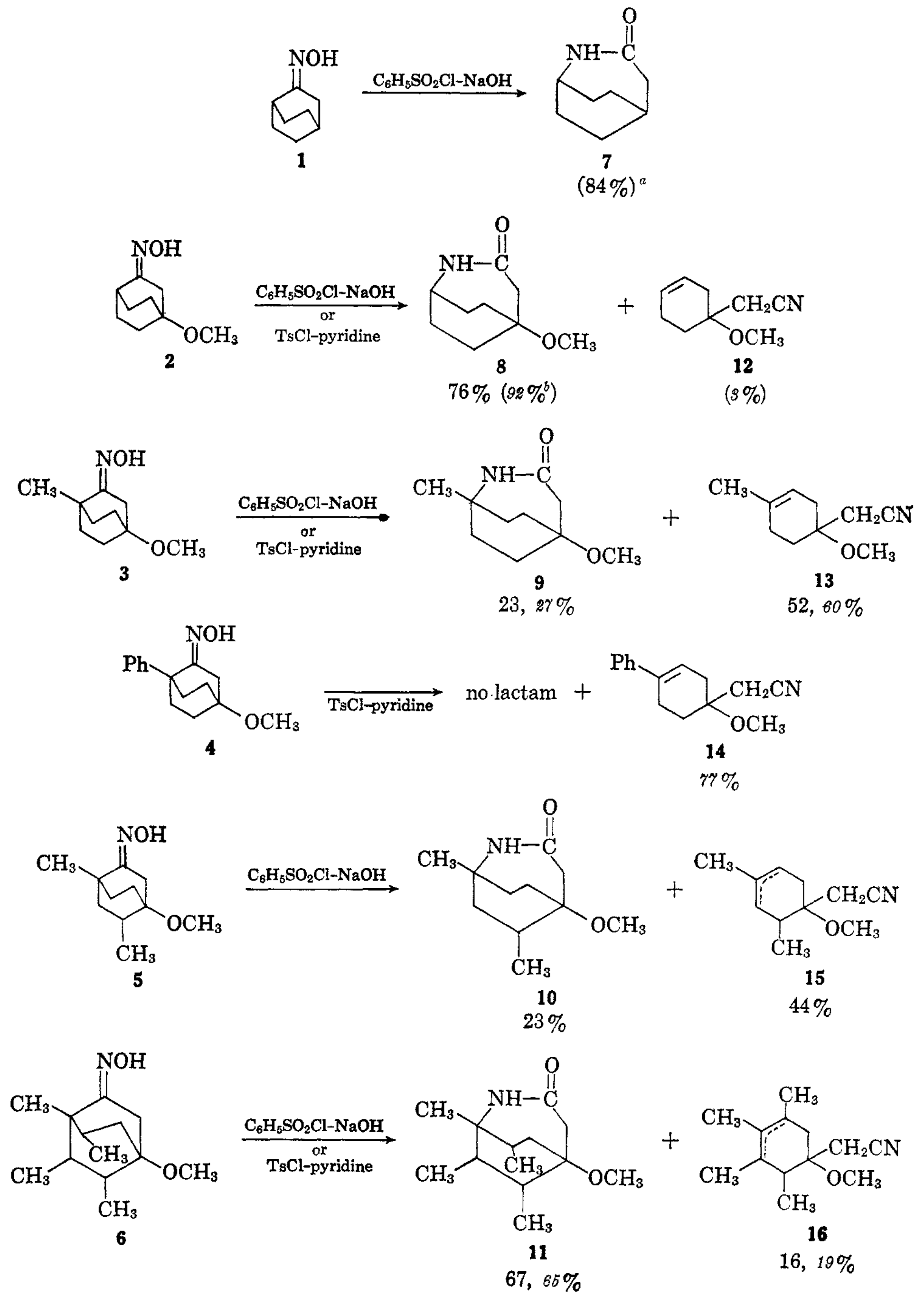
[8] W. D. Burrows and R. H. Eastman, *ibid.*, **79**, 3756 (1957).

[9] Drs. Y. Kurita and H. Nakata, personal communication; *cf.* Y. Kurita, M. Kashiwagi, and H. Saisho, *Nippon Kagaku Zasshi*, **86**, 578 (1965).

[10] L. G. Donaruma and W. Z. Heldt, *Org. Reactions*, **11**, 1 (1960).

[11] P. A. S. Smith, "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 483.

CHART I



[a] Crude yields are given in parentheses. [b] Yields by TsCl–pyridine are given in italics.

chloride solution of nitrile **13** with N-bromosuccinimide, followed by alkaline treatment of the resulting bromo compound, afforded *p*-tolylacetic acid (**18**).

Grob and co-workers[12a] have shown that the ratio of fragmentation to amide formation in the Beckmann rearrangement of ketoxime tosylates in 80% ethanol is not related to reaction rates but to the rates of solvolysis of the corresponding alkyl chlorides and consequently to the stability of the carbonium ion formed by cleavage, and concluded that fragmentation into nitriles occurs after the rate-determining step. They have also shown that reaction rates are related to migratory aptitudes of the migrating group and predicted that the rate-determining step of the Beckmann rearrangement of oxime tosylate in aqueous ethanol is an isomerization to an iminol tosylate.

One might illustrate the mechanism of the Beckmann rearrangement of bicyclo[2.2.2]octanone oximes with benzenesulfonyl chloride in aqueous alkali as depicted in Chart II.

Treatment of nitrile **12** and lactam **8** each with benzenesulfonyl chloride in aqueous sodium hydroxide under the conditions used in the present study gave only unchanged starting material.

The rearrangement of both bicyclo[2.2.2]octan-2-one oxime (**1**)[3] and 4-methoxybicyclo[2.2.2]octan-2-one oxime (**2**) yielded almost exclusively lactams. Substitution of a hydrogen atom by a methoxyl group in the 4-position of the bicyclo[2.2.2]octane system seems

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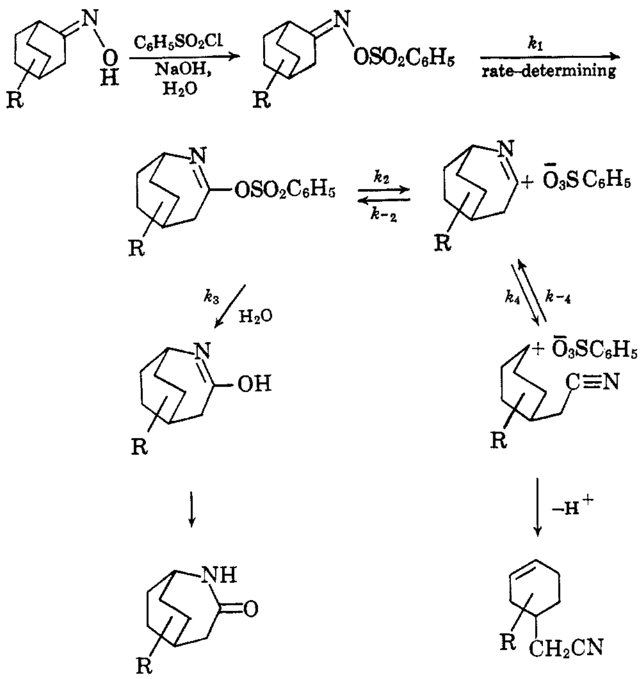
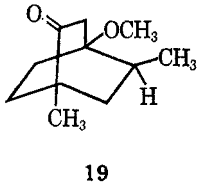
[12] (a) C. A. Grob, H. P. Fischer, W. Randenbusch, and J. Zergenyi, *Helv. Chim. Acta*, **47**, 1003 (1964); (b) R. W. Cottingham, *J. Org. Chem.*, **25**, 1473 (1960).

CHART II



to cause little effect on the ratio of lactam to nitrile formation (*cf.* Chart I). On the other hand, substitution of a hydrogen atom by a methyl group in the 1-position markedly increased the yield of nitriles. The rearrangement of 4-methoxy-1-methylbicyclo[2.2.2]-octan-2-one oxime (**3**) afforded about 55% of nitrile **13** and about 25% of lactam **9**, and that of 1,3-dimethyl-4-methoxybicyclo[2.2.2]octan-2-one oxime (**5**) furnished 44% of nitrile **15** and 23% of lactam **10**. The greater substituent effect was observed in the case of phenyl in the 1-position. Thus, rearrangement of 4-methoxy-1-phenylbicyclo[2.2.2]octan-2-one oxime (**4**) afforded only nitrile **14** in 77% yield. These results are compatible with an assumption[12] that the ratio of lactam formation to fragmentation decreases with the stability of the carbonium ion formed by cleavage.

The stereochemistry of 1,5-dimethyl-4-methoxybicyclo[2.2.2]octan-2-one[4] has been established[13] as shown in **19** by e.s.r. study. From this assignment and the mechanism of formation[4] of 4-methoxy-1,5,-6,7-tetramethylbicyclo[2.2.2]octan-2-one from *trans*-3-methyl-3-penten-2-one, configuration **20** is predicted for the latter ketone. Optical properties[14] of steroidal bicyclo[2.2.2]octanone compounds[15] prepared by an analogous reaction support the conclusion.



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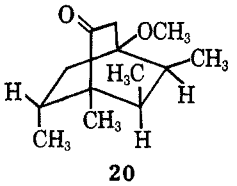

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Examination of Courtauld molecular model of 4-methoxy-1,5,6,7-tetramethylbicyclo[2.2.2]octan-2-one oxime (**6**) and 4-methoxy-1-methylbicyclo[2.2.2]octan-2-one oxime (**3**) revealed that it is much more difficult to open the 4-methoxy-1,5,6,7-tetramethylbicyclo-[2.2.2]octane ring than the 4-methoxy-1-methylbicyclo[2.2.2]octane ring because of nonbonded interactions involving steric hindrance of methyl groups. It was of interest to observe that the rearrangement of 4-methoxy-1,5,6,7-tetramethylbicyclo[2.2.2]octan-2-one oxime (**6**) afforded lactam **11** as a major product, whereas rearrangement of 4-methoxy-1-methylbicyclo-[2.2.2]octan-2-one oxime (**3**) afforded nitrile **13** as a major product (*cf.* Chart I). It is conceivable that the difficulty in opening (k_4) the bicyclic ring of the 4-methoxy-1,5,6,7-tetramethylbicyclo[2.2.2]octane system causes retardation of nitrile formation and hence increases the yield of lactam **11**.

Hill and Chortyk[16] have shown that the mechanism of the Beckmann rearrangement of 9-acetyl-*cis*-decalin oxime in acids such as sulfuric acid and polyphosphoric acid involves, in contrast to the rearrangement with *p*-toluenesulfonyl chloride in pyridine, fragmentation into acetonitrile and the 9-decalyl carbonium ion and recombination of these fragments leading to a lactam. The rearrangement of 4-methoxy-1-methylbicyclo[2.2.2]octan-2-one oxime (**3**) in polyphosphoric acid gave lactam **9** only in 5% yield. An analogous rearrangement of 4-methoxy-1,5,6,7-tetramethylbicyclo[2.2.2]octan-2-one oxime (**6**) in polyphosphoric acid gave a tarry mass from which no pure products could be isolated.

It has been observed[17] that the course of the Beckmann rearrangement depends upon the reagent employed. The Beckmann rearrangement of 4-methoxy-1-methylbicyclo[2.2.2]octan-2-one oxime (**3**) with *p*-toluenesulfonyl chloride in pyridine (or benzenesulfonyl chloride in alkali) afforded lactam **9** and nitrile **13** in 27 (or 23) and 60 (or 52)% yields, respectively. On the other hand, the rearrangement of the oxime **3** with phosphorus pentachloride in benzene afforded nitrile **13** in 93% yield.

Experimental Section[18]

4-Methoxybicyclo[2.2.2]octan-2-one.—To a magnetically stirred mixture of 70 g. (0.49 mole) of 4-acetylcyclohexanone and 160 g. (1.5 moles) of trimethyl orthoformate in 200 ml. of dry methanol was added 1 ml. of concentrated sulfuric acid with ice cooling. After the exothermal reaction had subsided, the yellow reaction mixture was allowed to warm to room temperature and stirred for 16 hr. To the dark red reaction mixture was added a methanolic sodium methoxide solution until the color disappeared. Methanol was removed by evaporation and 300 ml. of ether was added. The resulting precipitates were filtered off and the filtrate, after removal of the solvent by evaporation, was added to a mixture of 100 ml. of dry pyridine and 100 ml. of acetic anhydride. The mixture was heated at reflux under a nitrogen atmosphere for 5 hr. and then slowly distilled until the boiling point reached 130° and distillation ceased, taking about 3 hr. The residue was distilled *in vacuo* to afford 56.5 g. (69%) of **1-methoxy-4-(1-methoxyvinyl)cyclohexene**, b.p. 110–115° (20 mm.), lit.[19] b.p. 87–88.8° (2 mm.). The identity was established by the comparison of the infrared

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(13) G. A. Russell and K. Y. Chang, *J. Am. Chem. Soc.*, **87**, 4381 (1965).

(14) S. A. Latt, H. T. Cheung, and E. R. Blout, *ibid.*, **87**, 995 (1965).

(15) K. Morita, G. Slomp, and E. V. Jensen, *ibid.*, **84**, 3779 (1962).

(16) R. K. Hill and O. T. Chortyk, *ibid.*, **84**, 1064 (1962); also see R. T. Conley, *J. Org. Chem.*, **28**, 278 (1963).

(17) *Cf.* R. K. Hill and R. T. Conley, *J. Am. Chem. Soc.*, **82**, 645 (1960).

(18) Melting points were determined on Büchi melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 125 spectrophotometer. N.m.r. spectra were obtained with Varian A-60 instrument using deuteriochloroform, except where specified otherwise, as a solvent and tetramethylsilane as internal standard.

(19) I. N. Nazarov, G. P. Verkholtova, and L. D. Bergel'son, *Izv. Akad. Nauk SSSR*, 511 (1948); *Chem. Abstr.*, **43**, 2576*i* (1949).

spectra and the retention time of v.p.c. with those of an authentic sample of 1-methoxy-4-(1-methoxyvinyl)cyclohexene.[19]

To a stirred solution of 56.0 g. (0.33 mole) of the above material in 250 ml. of dry ether was added dropwise 2.0 g. (0.014 mole) of boron trifluoride etherate in 500 ml. of dry ether during a period of 2 hr. The mixture was stirred at room temperature for 16 hr. and then heated at reflux for 3 hr. The cooled dark red solution was washed once with 100 ml. of 1 *N* hydrochloric acid and twice with 100-ml. portions of water, dried over anhydrous sodium sulfate, and distilled. The fraction boiling at 120–125° (20 mm.) amounted to 23.4 g. (50%). The identity was established by comparison of the infrared spectra and the retention time on v.p.c. with those of an authentic sample of 4-methoxybicyclo[2.2.2]octan-2-one.[2]

4-Methoxybicyclo[2.2.2]octan-2-one Oxime (2).—To a solution of 7.1 g. of hydroxylamine hydrochloride and 4.1 g. of sodium hydroxide in 30 ml. of 30% aqueous ethanol was added 15.4 g. of 4-methoxybicyclo[2.2.2]octan-2-one. The mixture was then heated at 80° for 1 hr. The reaction mixture was cooled to −5° and the precipitated crystals were collected by filtration. Recrystallization from 20% aqueous ethanol afforded 14 g. of **2**, m.p. 114.5–115°.

Anal. Calcd. for $C_9H_{15}NO_2$: C, 63.88; H, 8.93; N, 8.28. Found: C, 63.53; H, 8.90; N, 8.06.

General Procedure for the Beckmann Rearrangement of Substituted Bicyclo[2.2.2]octan-2-one Oximes. A. With *p*-Toluenesulfonyl Chloride in Pyridine.[5]—To a magnetically stirred solution of 0.04 mole of the oximes in 20 ml. of dry pyridine was added dropwise a solution of 10 g. (0.05 mole) of *p*-toluenesulfonyl chloride in 20 ml. of the same solvent with ice cooling during a period of 20 min. The reaction was exothermic. The yellow solution was then allowed to warm to room temperature. After stirring at room temperature for 2 hr., the reaction mixture was heated at 60–70° and the stirring was continued for 13–17 hr. at that temperature. After cooling, the dark red reaction mixture was poured into a mixture of 150 g. of ice and 20 ml. of concentrated sulfuric acid and the mixture was stirred for 0.5 hr. Then, the mixture was extracted twice with 30-ml. portions of petroleum ether (b.p. 35–55°) and four times with 30-ml. portions of chloroform. The combined petroleum ether extract was washed once with water and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was combined with the nitrile fractions of the alumina chromatography (see below), and the mixture was distilled *in vacuo* to obtain nitriles. The yields of nitriles are listed in Chart I.

The residue of the above distillation was combined with the chloroform extracts and dried over anhydrous magnesium sulfate. After removal of the solvent, the yellow residue was dissolved in a small amount of methylene chloride and the solution was absorbed on an alumina (100 mesh, Sumitomo Chemical Co.) column packed in petroleum ether. Elution with petroleum ether gave nitriles. Further elution with ether gave lactams, which were recrystallized from benzene–ether. The physical constants of the resulting lactams are listed in Table I.

B. With Benzenesulfonyl Chloride in Aqueous Sodium Hydroxide Solution.[7]—To a vigorously stirred mixture of 0.01 mole of oximes in 20 ml. of 20% aqueous sodium hydroxide solution was added dropwise 3.0 g. (0.018 mole) of benzenesulfonyl chloride. The addition required 0.5–1 hr. and the temperature was not allowed to exceed 30°. After the exothermal reaction had subsided, the stirred reaction mixture was warmed and maintained at 50–60° for 2–10 hr. After cooling, the mixture was extracted four times with 30-ml. portions of petroleum ether and then four times with 30-ml. portions of chloroform. The petroleum ether extracts were combined, dried over anhydrous sodium sulfate, and concentrated. The residue was combined with the nitrile fractions from the alumina chromatography (see below) and the mixture was distilled *in vacuo* to afford nitriles. The residue of the above distillation was combined with the chloroform extracts and the mixture was dried over anhydrous magnesium sulfate and concentrated. The residue was dissolved in a small amount of methylene chloride and the solution was absorbed on an alumina column. Elution with petroleum ether gave nitriles. Further elution with ether afforded lactams, which were recrystallized from benzene–ether. The results are summarized in Chart I.

1-Methoxy-4-methyl-3-cyclohexenylacetonitrile (13).—It exhibited b.p. 105–107° (3.5 mm.); n^{20}D 1.4850; $\nu_{\max}^{\text{film}}$ 2255 (CN), 1102 cm.$^{-1}$ (OCH_3).

Anal. Calcd. for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.66; H, 9.17; N, 8.52.

1-Methoxy-2,4-dimethylcyclohexenylacetonitrile (15).—It exhibited b.p. 125–130° (15 mm.); n^{20}D 1.4875; $\nu_{\max}^{\text{film}}$ 2253 (CN), 1100 cm.$^{-1}$ (OCH_3).

Anal. Calcd. for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.93; H, 9.41; N, 7.86.

1-Methoxy-2,3,4,5-tetramethylcyclohexenylacetonitrile (16).—It exhibited b.p. 115–120 (12 mm.); $\nu_{\max}^{\text{film}}$ 2255 (CN), 1090–1105 cm.$^{-1}$ (OCH_3).

Anal. Calcd. for $C_{13}H_{21}NO$: N, 6.76. Found: N, 5.96.

1-Methoxy-4-phenyl-3-cyclohexenylacetonitrile (14).—It exhibited m.p. 74.5–75.0°; $\nu_{\max}^{\text{KBr}}$ 2270 cm.$^{-1}$ (CN).

Anal. Calcd. for $C_{15}H_{17}NO$: N, 6.16. Found: N, 6.02.

Reaction of 4-Methoxy-1-methylbicyclo[2.2.2]octan-2-one Oxime (3) with Polyphosphoric Acid.—A stirred mixture of 1.83 g. of oxime **3** and 40 g. of polyphosphoric acid was heated in an oil bath. After 10 min. at 120–130°, the mixture was allowed to cool. The contents of the reaction vessel were hydrolyzed by the addition of 70 g. of crushed ice and 500 ml. of 10% aqueous sodium hydroxide. The mixture was then extracted six times with 40-ml. portions of chloroform. The chloroform extracts were combined, washed once with water, and dried over anhydrous magnesium sulfate. After evaporation of the solvent, the residue was distilled *in vacuo* to afford 75 mg. of a ketone, b.p. *ca.* 90° (3 mm.), $\nu_{\max}^{\text{film}}$ 1745 cm.$^{-1}$.

The semicarbazone, which was prepared in a conventional way, exhibited m.p. 227.5–228.0° dec.

Anal. Calcd. for $C_{11}H_{17}N_3O_2$: C, 59.17; H, 7.68. Found: C, 59.02; H, 7.68.

The residue from the above distillation was chromatographed on alumina. Elution with ether gave 100 mg. of lactam **9**, m.p. 149.5–150°. The identity was established by the comparison of their infrared spectra and by mixture melting point.

The Rearrangement of 4-Methoxy-1-methylbicyclo[2.2.2]-octan-2-one Oxime (3) with Phosphorus Pentachloride.—To a magnetically stirred solution of 2.0 g. of oxime **3** in 30 ml. of thiophene-free benzene was added 2.0 g. of phosphorus pentachloride during a period of 15 min. at 0–5°. The resulting solution was allowed to warm and stirred at room temperature for 24 hr. The reaction mixture was then poured onto 100 g. of crushed ice and neutralized with aqueous sodium bicarbonate. After the addition of 30 g. of sodium chloride, the mixture was stirred for 30 min. and the benzene layer was separated. The water layer was shaken twice with 50-ml. portions of petroleum ether. The benzene and petroleum ether extracts were combined and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was distilled *in vacuo*. There was obtained 1.57 g. of nitrile **13**, b.p. 140–143° (19 mm.). The residue from the above distillation was chromatographed on alumina. Elution with petroleum ether gave 0.13 g. of nitrile **13**. The total yield of nitrile was 1.70 g. (93%). Further elution with ether afforded 0.04 g. (2%) of lactam **9**, m.p. 149–150°.

Hydrolysis of 4-Methoxy-2-azabicyclo[3.2.2]nonan-3-one (8).—To a mixture of 1.2 ml. of concentrated sulfuric acid and 1.5 ml. of water was added 0.75 g. of **8**, and the mixture was heated at 150° for 5 hr. Then, 1.5 ml. of water was added and the mixture was heated at 150° for 15 hr. After cooling, the reaction mixture was neutralized with an aqueous barium hydroxide solution. Precipitated barium sulfate was removed centrifugally and the solution was passed through a column of a cation-exchange resin (Amberlite IR-120). Elution with 2 *N* ammonia solution and crystallization from a small amount of water afforded 0.19 g. of **4-aminocyclohexylideneacetic acid**, m.p. 285° dec.

Anal. Calcd. for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03. Found: C, 62.24; H, 8.43; N, 8.70.

The N-acetate, which was prepared in a conventional way, melted at 199° (from methanol).

Anal. Calcd. for $C_{10}H_{15}NO_3$: C, 60.89; H, 7.67; N, 7.10. Found: C, 60.80; H, 7.70; N, 6.92.

***p*-Tolylacetic Acid (18) from 1-Methoxy-4-methylcyclohexenylacetonitrile (13).**—A carbon tetrachloride solution of a mixture of 120 mg. of 1-methoxy-4-methylcyclohexenylacetonitrile (**13**) and 130 mg. of N-bromosuccinimide was heated at reflux for 18 hr. After removal of the precipitates by filtration, the solvent was evaporated. The resulting red residue was dissolved in 5 ml. of ethanol and to that solution was added 2 ml. of 10% aqueous sodium hydroxide solution. The black solution was heated for 2 hr. After cooling, active charcoal was added and the mixture was heated for a few minutes. After filtering off the charcoal, the solution was evaporated to a volume of *ca.* 2 ml. and acidified with 6 *N* hydrochloric acid. On cooling, there was obtained 65 mg. of **18**, m.p. 88-92°, lit.[20] m.p. 94°. The infrared spectrum was identical with that of *p*-tolylacetic acid.[21]

Acknowledgment.—We wish to thank Professor G. A. Russell and Dr. Y. Kurita for supplying us with unpublished data relating to their e.s.r. experiments. We are indebted to a member of the analytical section of this laboratory for the microanalyses and physical determinations.

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[20] A. L. Wilds and A. L. Meader, Jr., *J. Org. Chem.*, **13**, 763 (1948).

[21] The Sadtler Standard Spectra, Vol. VIII, Midget Ed., Sadtler Research Laboratories, Philadelphia, Pa., 1962, Compound 6517.

Ultraviolet Irradiation of Carbonyl Compounds in Cyclohexene and 1-Hexene

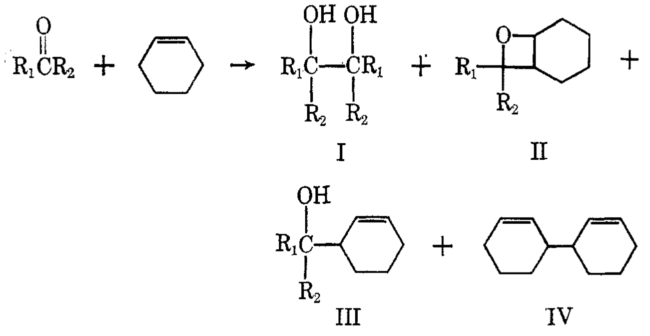
JERALD S. BRADSHAW

Chevron Research Company, Richmond, California

Received May 24, 1965

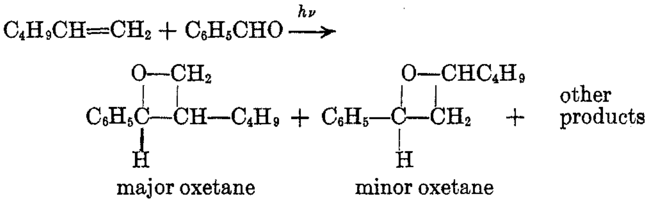
The photolysis of benzophenone and benzaldehyde in cyclohexene and 1-hexene gave four products—pinacol, oxetane, alcohol, and hydrocarbon dimer. Acetone and acetophenone yielded oxetane, alcohol, and bicyclohexenyl when irradiated in cyclohexene. The yields of oxetane from these reactions were smaller than those obtained with more highly substituted olefins. These differences in yields may be attributed to the greater stability of the more highly substituted diradical intermediate V.

Carbonyl compounds can undergo a variety of photolytic reactions in solution. Phenyl ketones are readily reduced to pinacols in the presence of hydrogen donors.[1-3] Alcohols and hydrocarbon dimers resulting from radical reactions are produced when aliphatic ketones react with cyclohexene[4] and are the byproducts of the benzophenone–alkylbenzene reaction.[2] When irradiated in di- and greater substituted acyclic and substituted cyclic olefins, carbonyl compounds react with the olefin to give oxetanes in high yields.[5-7] We have isolated from the photolysis of carbonyl compounds in α-olefins and cyclohexene, not a single product, but rather four products—pinacol, oxetane, alcohol, and hydrocarbon dimer. Others may have also been formed. Some of these products have obviously been overlooked in the past. For example, oxetane products were not reported for the irradiation of both acetone and benzophenone in cyclohexene.[4,6]

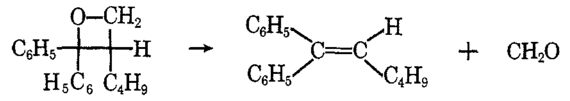


The carbonyl compounds were dissolved in the olefin and irradiated until most of the carbonyl had reacted. When benzophenone was used, benzopinacol separated during the reaction. The other products were isolated by chromatography on alumina. Table I records the results.

The oxetanes were characterized by their distinctive n.m.r. spectra (Figure 1). A mixture of *cis*- and *trans*-oxetane isomers was formed when benzaldehyde was irradiated in the presence of 1-hexene. The doublet at δ 5.85 has been tentatively assigned to the *cis* isomer, while that at δ 5.35 has been assigned to the *trans* isomer (Figure 1).[8] *trans*-Oxetane predominated by about 2 to 1. In addition to the major doublets between δ 5 and 6, the n.m.r. spectrum of the first oxetane fraction contained a small triplet at δ 5.5. This could correspond to a small amount of oxetane with the oxygen next to the $-CHC_4H_9$ group.[7]



The oxetanes from cyclohexene gave molecular ions at the expected *m/e* in the mass spectrometer, while those prepared from 1-hexene gave large peaks at the expected mass less 30, corresponding to loss of formaldehyde. This latter is due to either a thermal decomposition in the 210° inlet system or occurs in the ionizing beam of the mass spectrometer. Such a cleavage was reported by Bardot in the pyrolysis of 2,2-diethyloxetane.[9]



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[1] For a review, see A. Schonberg and A. Mustafa, *Chem. Rev.*, **40**, 181 (1947).

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[3] (a) A. Becket and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963); (b) G. Porter and P. Suppon, *Proc. Chem. Soc.*, 191 (1964).

[4] P. de Mayo, J. B. Stothers, and W. Templeton, *Can. J. Chem.*, **39**, 488 (1961).

[5] G. Büchi, C. G. Inman, and E. S. Lipinsky, *J. Am. Chem. Soc.*, **76**, 4327 (1954).

[6] D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964).

[7] N. C. Yang, M. Nussim, M. J. Jorgenson, and S. Murov, *ibid.*, 3657 (1964).

[8] See N. S. Bhacca and D. H. Williams ("Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p. 50) for dihedral angle dependence of *J*. The doublet at δ 5.85 has a *J* of about 9 c.p.s. which corresponds to either a 0 or 145° dihedral angle. Models show that the *cis* isomer has a dihedral angle of 0°. The *trans* isomer has a dihedral angle of 120°, corresponding to the *J* value of 6 c.p.s. observed for the δ 5.35 doublet.

[9] A. Bardot, *Ann. Chim.* (Paris), **11**, 519 (1939).