Formation of Bicyclo[2.2.0]hexane Derivatives by the Ring Contraction of Bicyclo[3.2.0]heptanones

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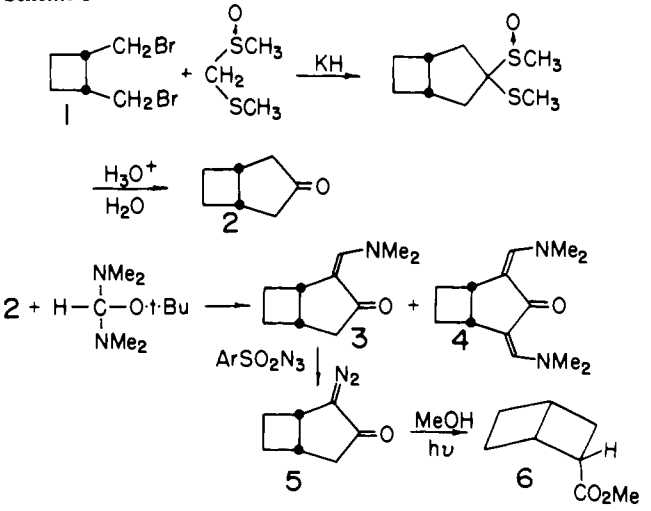
Abstract: Ring contraction via the photochemical Wolff rearrangement of diazo ketones has been applied to several *cis*-bicyclo[3.2.0]heptan-2- and -3-ones to give substituted *cis*-bicyclo[2.2.0]hexanes. The ring contraction was unsuccessful with *trans*-bicyclo[3.2.0]heptan-3-one. The diazo ketone was unstable and in methanol gave methyl cyclopent-2-en-1-acetate.

Despite the large strain energy of bicyclo[2.2.0]hexane (~55 kcal/mol),[2] it does not undergo acid-catalyzed ring opening and only slowly reacts with bromine.[3] The thermal rearrangement of bicyclo[2.2.0]hexane[4] may involve the same intermediate or activated complex as the degenerate Cope rearrangement of 1,5-hexadiene,[5] and a study of substituent effects may provide further information concerning this rearrangement. The transition metal catalyzed rearrangements of bicyclohexane and related compounds[6] lead to organometallic intermediates which are useful in studying the course of the rearrangements. For these and other reasons, it would be helpful to be able to prepare bicyclohexanes having a variety of patterns of substitution.

The methods available for the preparation of bicyclohexane derivatives are rather limited. The most generally applicable method involves the Diels–Alder reaction of cyclobutadiene with alkenes or alkynes followed by reduction of the C–C double bonds,[7] but this only leads to 2- or 2,3-disubstituted derivatives. Several 1,4-disubstituted compounds are available via the pseudo-Favorskii ring contraction of 1,4-dichloro-7-norbornanone.[8] These procedures are limited in the substitution patterns which they allow.

One of the potentially attractive methods for the preparation of bicyclo[2.2.0]hexanes is the ring contraction of the diazo ketones derived from bicyclo[3.2.0]heptanones. The latter are frequently readily prepared by methods such as the photochemical addition of an alkene to a cyclopentenone.[9] Since this method had previously only been applied to a tricyclic case,[10] the first attempt made use of bicyclo[3.2.0]heptan-3-one (**2**). It was readily prepared from *cis*-1,2-dibromomethylcyclobutane (**1**) via condensation with methyl methylsulfinylmethyl sulfide[11] as shown in Scheme I. The ketone **2** reacted with a small excess of bis(dimethylamino)-*tert*-butoxymethane[12] to give a mixture of mono (**3**) and bis enamino ketones (**4**). The formation of **4** could be repressed by using stoichiometric quantities of the reactants. The reaction of **3** with tosyl azide proceeded rather slowly to give the diazo ketone **5**, but the reaction could be accelerated by the use of the more reactive *p*-nitrobenzenesulfonyl azide. The diazo ketone was found to be quite stable and could be purified by chromatography over alumina. Photolysis of **5** in methanol gave methyl bicyclo[2.2.0]hexane-*endo*-2-carboxylate (**6**), which was identified by comparison with an authentic sample.[13]

Scheme I



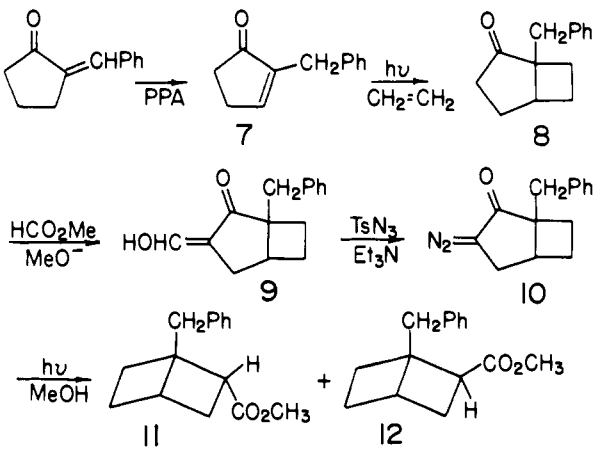
Although the conversion of **2** to **5** proceeded in only modest yield (48 and 40% for the two steps), the method appeared promising. Since the difficulty with the conversion of **2** to the enamino ketone could be minimized by the use of a bicyclo[3.2.0]heptan-2-one, these compounds were next examined.

2-Benzylcyclopentenone (**7**) was readily obtained via the acid-catalyzed isomerization of 2-benzylidenecyclopentanone.[14] The photochemical addition of ethylene to **7** proceeded well to give 1-benzylbicyclo[3.2.0]heptan-2-one (**8**). The reaction of **8** with methyl formate gave the formyl derivative (**9**) which could be converted to the diazo ketone (**10**) via reaction with tosyl azide. Photolysis of **10** gave a mixture of *endo*- and *exo*-methyl 1-benzylbicyclo[2.2.0]hexane-2-carboxylates (**11** and **12**) in a 3:1 ratio (Scheme II).

In this case, the conversion of the ketone **8** to the diazo ketone and then to the ring-contracted esters proceeded very well giving the overall yield of 45% for the three steps. The ring contraction of **5** gave only the endo ester corresponding to the protonation of the intermediate ketene from the less hindered side.[15] The reaction of **10** gave both the endo and exo esters because the 1-benzyl group interferes with exo attack on the ketene, thus making the steric factors approximately equal for the two directions of attack.

The reaction also was successful when the side chain contained a functional group (Scheme III). The cyclopentenone with an acetylenic side chain, **13**,[16] underwent the photo-

Scheme II



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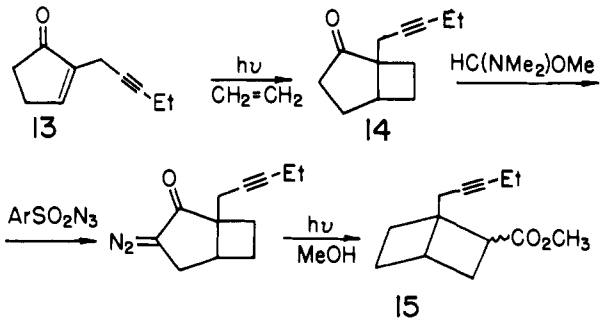
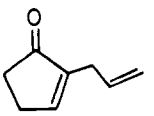
Scheme III



chemical cycloaddition with ethylene to give the ketone **14.** Conversion to the diazo ketone followed by photolysis in methanol again led to a mixture of epimeric esters, **15.** On the other hand, the use of an allylic side chain as in **16** was un-



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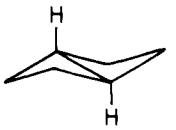
successful because the initial photochemical reaction led to intramolecular reaction rather than an intermolecular reaction with ethylene.

All of the bicyclo[2.2.0]hexanes which have thus far been prepared have a cis ring junction. It is also possible for the junction to be trans, giving **17.** This hydrocarbon is of unusual



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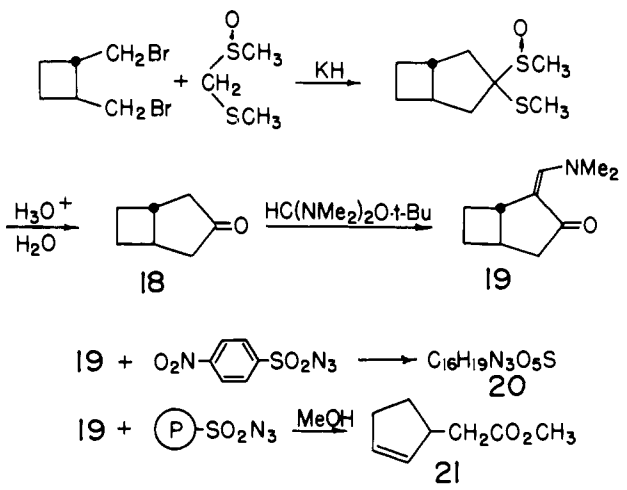
interest since (a) by thermolysis it would lead directly to the chair cyclohexane 1,4 diradical which has been implicated in the thermolysis of *cis*-bicyclo[2.2.0]hexane,[4] and which has the geometry of the activated complex for the degenerate Cope rearrangement of 1,5-hexadiene;[5] (b) the twist-bent[17] C-C central bond should be more susceptible to electrophilic attack than other cyclobutanes, and thus might have a reactivity comparable to that of cyclopropanes;[18] (c) its energy and geometry would give information concerning the potential function for bending cyclobutane past 35°.[19] We have therefore explored the ring contraction route to the trans isomer.

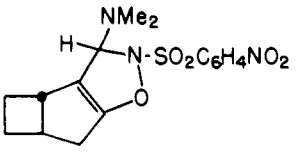
trans-Bicyclo[3.2.0]heptan-3-one (**18**) was prepared in the same fashion as previously described for the cis ketone (**2**) (Scheme IV). The yields in the two cases were comparable. Conversion to the enamino ketone **19** proceeded without dif-

Scheme IV



ficulty and in good yield (82%). The bis enamino ketone was not formed in this case. When **19** was treated with tosyl azide in dichloromethane at 0 °C, a yellow color at first appeared, but then bubbles of gas formed almost immediately, and workup of the reaction solution gave only a tarry residue. Tosyl azide did not react with **19** at an appreciable rate below 0 °C.

When **19** was treated with the more reactive *p*-nitrobenzenesulfonyl azide in ether, a yellow precipitate formed. Recrystallization gave yellow-orange crystals, mp 179 °C. The NMR spectrum showed the presence of an aromatic ring at δ 8.11 (q, 4 H), a singlet at δ 6.43 (1 H), and a singlet at δ 3.19 (6 H) in addition to broad absorption at δ 1.50–2.90 (8 H). The IR spectrum showed strong absorption at 1530 cm^{-1} and was blank from 1550 to 2200 cm^{-1}. Elemental analysis indicated $C_{16}H_{19}N_3O_5S$, corresponding to a 1:1 adduct of **19** and the azide, less the elements of nitrogen. When the reaction was repeated in methanol solution, the same product was formed, suggesting that a ketene was not formed as an intermediate. The absence of a carbonyl band in the IR spectrum suggests a structure such as **20.**



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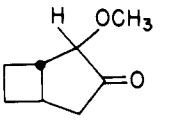
Roush, Feitler, and Rebek[20] have reported the preparation and use of a polymeric sulfonyl azide which allowed the products of the reaction to be separated from the insoluble sulfonyl azide residue via filtration or decantation. The trans-fused enamino ketone **19** was treated with an excess of the polymeric azide in a mixture of dichloromethane and methanol. Gas was evolved during the reaction. The crude product was separated by gas chromatography to yield two compounds in a ratio of 3:1. The major product was found to be methyl 2-cyclopentene-1-acetate (**21**). The minor product appeared to be a methyl ether derived from the unrearranged bicyclo[3.2.0]heptane system as indicated by the similarity in the NMR and IR spectra and the observation of a methoxy singlet at δ 3.22. The elemental analysis indicated $C_8H_{12}O_2$. The structure, **22,** appears to fit these data.



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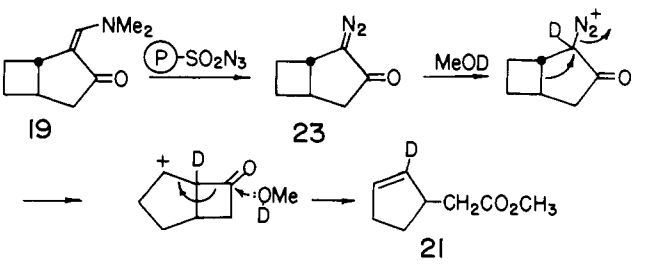
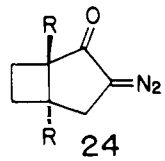
The formation of these products was of interest, and therefore was further examined by carrying out the reaction in methanol-*d*. The cyclopentenacetic ester was found to be deuterium labeled at the double bond, suggesting the path shown in Scheme V. After the formation of the diazo ketone, protonation by methanol could occur either before or after the loss of nitrogen. Two successive bond shifts would lead to **21** with the deuterium at the indicated position. The minor com-

Scheme V



ponent, **22,** could be formed by attack of methanol on the initial protonated species before rearrangement.

The difference in behavior between the cis- and trans-fused enamino ketones suggests that the difficulty with the trans diazo ketone **23** may be the placement of the diazo group adjacent to the ring juncture, The reaction may be more successful with the 3-diazo 2-ketone **24,** which will require alkyl substitution at the bridgehead in order to avoid epimerization. The synthesis of **24** is currently being undertaken.



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Experimental Section

***cis*-Bicyclo[3,2.0]heptan-3-one (2).** To a 1-L three-necked flask fitted with a mechanical stirrer and dropping funnel were added 34.3 g (0.86 mol) of potassium hydride (24.4% dispersion in oil) and 500 mL of tetrahydrofuran which had been distilled from lithium aluminum hydride. The stirred suspension was cooled to 0 °C under nitrogen and 38 g (0.31 mol) of methyl methylsulfinylmethyl sulfide in 70 mL of tetrahydrofuran was added dropwise over 1 h. The flask was warmed to 20 °C and 74 g (0.31 mol) of *cis*-1,2-bis(bromomethyl)-cyclobutane (**I**)[21] was added dropwise over 1 h. After stirring for 20 h, the flask was immersed in ice, 300 mL of dichloromethane was added, and the solution was filtered. The solvent was removed using a rotary evaporator. The residue was dissolved in 300 mL of acetone and 14 mL of 9 N sulfuric acid, stirred at room temperature for 20 h, and heated to reflux for 3 h. Most of the solvent was removed and the residue was dissolved in ether. It was washed with aqueous sodium bicarbonate, water, and saturated sodium chloride solutions and dried over magnesium sulfate. Distillation gave 15.6 g (47%) of the cis ketone, bp 98–102 °C (60 mm). The IR carbonyl band was at 1743 cm^{-1}. The structure was confirmed by comparison with an authentic sample.[22]

***trans*-Bicyclo[3,2.0]heptan-3-one (18).** The procedure for the cis ketone was employed using 23 g of potassium hydride and 50 g of *trans*-1,2-bis(bromomethyl)cyclobutane.[23] There was obtained 13 g (58%) of the trans ketone, bp 100 °C (60 mm). The IR carbonyl band was 1741 cm^{-1}. The structure was confirmed by comparison with an authentic sample.[23]

2-Benzylcyclopentenone (7). The compound was prepared by a modification of the procedure of Conia and Amice.[14] A mixture of 50 g (0.29 mol) of benzylidenecyclopentanone and 250 g of polyphosphoric acid was stirred at 100 °C for 3 h. The resulting dark brown, viscous mixture was dissolved in boiling water and steam distilled, giving about 2 L of distillate. The cooled distillate was extracted with ether and the ether solution was dried over magnesium sulfate. Removal of the solvent gave 17.5 g (35%) of 2-benzylcyclopentenone which appeared pure by GC and had NMR bands ($CDCl_3$) at δ 7.24 (m, 5 H), 7.14 (m, 1 H), 3.49 (m, 2 H), 2.45 (m, 4 H).

1-Benzylbicyclo[3.2,0]heptan-2-one (8). In a photolysis apparatus equipped with a vacuum-jacketed, water-cooled Pyrex immersion well was placed a solution of 17.5 g (0.10 mol) of 2-benzylcyclopentenone (**7**) in 525 mL of acetone. The solution was degassed by flushing with ethylene. With both the ethylene and the cooling water flowing briskly, the entire assembly was immersed in a dry ice–acetone bath. When the solution temperature reached −78 °C, the ethylene flow was reduced. Photolysis was effected using a Hanovia 450-W mercury lamp, and the reaction was monitored by GC. The reaction was complete in 20–24 h. The solution was concentrated and the product was distilled, bp 93–95 °C (0.1 mm), giving 14.7 g (84%) of the ketone. The IR spectrum (CCl_4) had bands at 1730 and 1450 cm^{-1}; the ^1H NMR spectrum (CCl_4) had bands at δ 7.17 (m, 5 H), 3.04 (d, J = 13 Hz, 1 H), 2.78 (m, 1 H), 2.73 (d, J = 13 Hz, 1 H), 2.59 (q, J = 10 Hz, 1 H), 2.21–1.91 (m, 4 H), 1.63 (m, 2 H), and 1.45 (m, 1 H), and the ^{13}C NMR spectrum ($CDCl_3$, ^1H decoupled) had bands at δ 137.7, 129.4, 128.0, 126.1, 54.0, 40.1, 38.8, 37.1, 28.0, 25.7, and 21.3.[24] MS: molecular ion at *m/e* 200. Anal. ($C_{14}H_{16}O$) C, H.

1-(2-Pentynyl)bicyclo[3,2.0]heptan-2-one (14). A solution of 2.3 g (0.016 mol) of 2-(2-pentynyl)-2-cyclopentenone[16] in 525 mL of hexane was irradiated at 0 °C with a 450-W Hanovia mercury lamp while bubbling ethylene through the solution. After 22 h, the solution was concentrated and purified by chromatography using activity 1 basic alumina and eluting with 1:1 pentane–ether to give 1.0 g (37%) of the ketone. The IR spectrum (CCl_4) had a carbonyl band at 1740 cm^{-1}; the ^1H NMR spectrum had bands at δ 2.95 (m, 1 H), 2.76 (m, 1 H), 2.37 (m, 3 H), 1.96–2.22 (m, 4 H), 1.67–1.96 (m, 4 H), 1.10 (t, J = 7.5 Hz, 3 H); the ^{13}C spectrum ($CDCl_3$, ^1H decoupled) had bands at δ 82.4, 75.4, 51.4, 38.9, 36.8, 26.3, 26.1, 23.1, 21.3, 14.0, and 12.0.[24] MS: molecular ion at *m/e* 176. Anal. ($C_{12}H_{16}O$) C, H.

Reaction of *cis*-Bicyclo[3.2.0]heptan-3-one (2) with Bis(dimethylamino)-*tert*-butoxymethane. A mixture of 2.0 g (0.018 mol) of *cis*-bicyclo[3.2.0]heptan-3-one (**2**) and 4.75 g (0.27 mol) of bis(dimethylamino)-*tert*-butoxymethane was stirred for 24 h at 80 °C, at which time GC analysis indicated the absence of starting material. Volatile material was removed by warming under reduced pressure (0.1 mm) and the residue was distilled, giving two fractions. The first, bp 125–135 °C (0.1 mm) (1.2 g), was a viscous, yellow liquid whereas the second, bp 190–210 °C (0.1 mm) (1.3 g), solidified in the condenser. The first fraction was purified by preparative GC on a 2-ft Apiezon column at 170 °C and was found to be 2-[(dimethylamino)-methylene]-*cis*-bicyclo[3.2.0]heptan-3-one (**3**). The IR spectrum (CCl_4) had bands at 1680 and 1584 cm^{-1}; the ^1H NMR spectrum ($CDCl_3$) had bands at δ 7.50 (s, 1 H), 3.5–3.8 (m, 1 H), 3.02 (s, 6 H), 1.6–2.6 (m, 7 H). MS: molecular ion at *m/e* 165. Anal. ($C_{10}H_{15}NO$) C, H; N: calcd, 8.5; found, 7.9.

The second fraction was recrystallized from ether–dichloromethane to give yellow crystals, mp 113–114 °C, and was found to be 2,4-bis-[dimethylamino)methylene]-*cis*-bicyclo[3.2.0]heptan-3-one (**4**). The IR spectrum (CCl_4) had a band at 1604 cm^{-1}; the ^1H NMR spectrum ($CDCl_3$) had bands at δ 7.12 (s, 2 H), 3.4–3.8 (m, 2 H), 2.95 (s, 12 H), 2.2–2.6 (m, 2 H), 1.6–2.0 (m, 2 H). MS: molecular ion at *m/e* 220. Anal. ($C_{13}H_{20}N_2O$) C, H, N.

The proportion of mono adduct could be improved by using a 1:1 ratio of reactants (3.6 and 5.7 g, respectively). Distillation gave 2.6 g (48%) of the mono adduct, bp 110 °C (0.07 mm).

2-Diazo-*cis*-bicyclo[3.2.0]heptan-3-one (5). A solution of 0.5 g (3 mmol) of 2-[(dimethylamino)methylene]-*cis*-bicyclo[3.2.0]heptan-3-one (**3**) in 30 mL of diethyl ether was cooled to 0 °C and 0.6 g (3 mmol) of tosyl azide was added dropwise with stirring. After 20 h at room temperature the solvent was removed under reduced pressure and the residue was chromatographed over basic alumina (activity II) and eluted with 2:1 pentane–ether. The yellow fraction was concentrated to give 0.16 g (40%) of the diazo ketone. The IR spectrum had bands at 2080 and 1678 cm^{-1}, and the ^1H NMR spectrum had bands at δ 3.8–4.0 (m, 1 H), 3.17 (t, 2 H), 1.8–2.8 (m, 5 H). The reaction of the enamino ketone with *p*-nitrobenzenesulfonyl azide proceeded more rapidly (3 h), but the yield was unchanged.

Methyl *cis*-Bicyclo[2.2.0]hexane-*endo*-2-carboxylate (6). A solution of 0.25 g of 2-diazo-*cis*-bicyclo[3.2.0]heptan-3-one (**5**) in 10 mL of dry methanol was placed in a Pyrex test tube fitted with a drying tube and surrounded by a water bath at 20 °C. The solution was irradiated for 2 h with a 450-W Hanovia mercury lamp placed 6 in. away. The solvent was removed under reduced pressure and the residue was purified by GC (4-ft 30% SE-30 column at 90 °C). Only one compound was found (17 min) and it was shown to be methyl *cis*-bicyclo[2.2.0]hexane-*endo*-2-carboxylate by comparison with an authentic sample.[13] The IR spectrum (CCl_4) had a carbonyl band at 1735 cm^{-1}; the ^1H NMR spectrum ($CDCl_3$) had bands at δ 3.62 (s, 3 H), 1.8–3.5 (m, 9 H). MS: molecular ion at *m/e* 140. Anal. ($C_8H_{12}O_2$) C, H.

Methyl 1-Benzylbicyclo[2.2.0]hexane-2-carboxylate (11, 12). To a dry 100-mL three-necked flask equipped with a mechanical stirrer and a drying tube were added 60 mL of dry ether and 1.4 g (0.029 mol) of a 50% sodium hydride dispersion in oil. While stirring with ice-bath cooling there was added 12 drops of methanol followed by the dropwise addition of an ether (20 mL) solution of 5.7 g (0.029 mol) of 1-benzylbicyclo[3.2.0]heptan-2-one (**8**) and 26 mL of methyl formate. The mixture was stirred overnight as the ice in the cooling bath melted. Methanol (5 mL) was added and stirring was continued for 15 min. Water was added and the ether layer was separated. The ether layer was washed with water and the combined aqueous layers were extracted with ether. The aqueous layer was acidified to pH 1 with 6 N hydrochloric acid and extracted with ether. The ether solution was washed with brine, dried, and concentrated to give 5.5 g (84%) of crude 1-benzyl-3-formylbicyclo[3.2.0]heptan-2-one (**9**). The IR spectrum (neat) had bands at 1690, 1660, and 1595 cm^{-1}.

The formyl ketone **9** (4.9 g, 0.021 mol) was dissolved in 50 mL of

methylene chloride and 4.6 g (0.046 mol) of triethylamine was added. This solution was cooled in an ice-salt bath and a methylene chloride solution containing 0.021 mol of tosyl azide was added slowly. The mixture was stirred for 2 h as the ice in the cooling bath melted. Potassium hydroxide solution (22 mL, 6%) was added and stirring was continued for 15 min. The layers were separated and the aqueous layer was extracted with methylene chloride. The solution was washed twice with 1.5% potassium hydroxide solution and once with water and dried. It was concentrated and then passed through activity I basic alumina with 1:1 pentane–ether, giving 4.3 g (89%) of yellow 1-benzyl-3-diazobicyclo[3.2.0]heptan-2-one (**10**). The IR spectrum (neat) had bands at 2075 and 1660 cm^{-1}.

The diazo ketone **10** (4.3 g, 0.019 mol) was dissolved in 150 mL of methanol and was irradiated with ice-bath cooling using a Hanovia 450-W mercury lamp. The reaction was complete after 4 h. The product, methyl 1-benzylbicyclo[2.2.0]hexane-2-carboxylate, was isolated by column chromatography using activity I basic alumina and 1:1 pentane–ether, giving 2.9 g (60%) of a 3:1 mixture of **11** and **12**. The analytical sample was further purified by GC using a 7-ft SE-30 column at 150 °C. The IR spectrum (neat) had bands at 1730 and 1430 cm^{-1}; the ^1H NMR spectrum ($CDCl_3$) had bands at δ 7.3 (m, 5 H), 3.68, 3.60 (s, 3:1, 3 H), 3.39, 3.06 (t, 1:3, 1 H), 2.5–2.9 (m, 3 H), 1.7–2.4 (m, 6 H). MS: molecular ion at *m/e* 226. Anal. ($C_{15}H_{18}O$) C, H.

Methyl 1-(2-Pentynyl)bicyclo[2.2.0]hexane-2-carboxylate (15). A mixture of 1.5 g (8.6 mmol) of 1-(2-pentynyl)bicyclo[3.2.0]heptan-2-one (**14**) and 2.6 g (19 mmol) of bis(dimethylamino)methoxymethane was heated under nitrogen at 60 °C for 20 h. Distillation gave 1.15 g (58%) of the enamino ketone, bp 146–153 °C (0.1 mm). IR (neat): 1680, 1500 cm^{-1}.

A solution of 1.15 g (5 mmol) of the enamino ketone in 20 mL of methylene chloride was cooled to −70 °C and 1.5 g (6.5 mmol) of *p*-nitrobenzenesulfonyl azide was added. The solution was allowed to warm to room temperature with stirring over 3 h. The solution was concentrated, and the diazo ketone was taken up in pentane. Chromatography using activity I basic alumina and 1:1 ether–pentane gave 0.9 g (90%) of 1-(2-pentynyl)-3-diazobicyclo[3.2.0]heptan-2-one. IR (neat): 2075, 1665 cm^{-1}.

A solution of 0.9 g of the diazo ketone in 40 mL of methanol was irradiated for 3 h with a 450-W Hanovia mercury lamp. The solvent was removed and the residue was chromatographed using activity I basic alumina and ether–pentane, giving 0.5 g (54%) of methyl 1-(2-pentynyl)bicyclo[2.2.0]hexane. The IR spectrum (CCl_4) had bands at 1733 and 1435 cm^{-1}. The ^1H NMR spectrum ($CDCl_3$) indicated a mixture of endo and exo isomers in a 4:3 ratio: δ 3.68, 3.67 (4:3, 3 H), 3.33 (m, 1 H), 1.70–2.65 (m, 11 H), 1.14 (m, 3 H). MS: molecular ion at *m/e* 206. Anal. ($C_{13}H_{18}O_2$) C, H.

2-[(Dimethylamino)methylene]-*trans*-bicyclo[3.2.0]heptan-3-one (19). A mixture of 2.8 g (0.026 mol) of *trans*-bicyclo[3.2.0]heptan-3-one (**18**) and 5.3 g (0.031 mol) of bis(dimethylamino)-*tert*-butoxymethane was stirred for 48 h at 80 °C, after which time GC analysis showed the absence of **18**. Distillation gave 3.4 g (82%) of **19**, bp 96–99 °C (0.04 mm), which solidified in the condenser. Recrystallization from ether–hexane gave the pure enamino ketone, mp 86–87 °C. The IR spectrum had bands at 1695 and 1602 cm^{-1}; the ^1H NMR spectrum had bands at δ 7.01 (s, 1 H), 2.92 (s, 6 H), 1.50–2.50 (complex, 8 H). MS: molecular ion at *m/e* 165. Anal. ($C_{10}H_{15}NO$) C, H, N.

Reactions of 2-[(Dimethylamino)methylene]-*trans*-bicyclo[3.2.0]heptan-3-one (19). A. With Tosyl Azide in Methylene Chloride. A solution of 0.5 g of **19** in 30 mL of methylene chloride was cooled to 0 °C and 0.6 g of tosyl azide was added dropwise. The stirred solution was allowed to warm to room temperature and bubbles of gas were evolved during the first hour. Removal of the solvent under reduced pressure with no heat supplied led to a tarry residue. Attempted chromatography over alumina did not lead to any products. When the infrared spectrum of the solution was taken shortly after the addition of the tosyl azide, a small band at 2080 cm^{-1} was found along with the azide band at 2120 cm^{-1}.

B. With *p*-Nitrobenzenesulfonyl Azide. A stirred solution of 1.0 g of **19** in 30 mL of diethyl ether was cooled to 0 °C and 1.39 g of *p*-nitrobenzenesulfonyl azide in 10 mL of dichloromethane was added dropwise over 10 min. The solution was allowed to warm to room temperature and was stirred for 3 h. The yellow precipitate (2 g) was removed by filtration and recrystallized from dichloromethane–ether to give yellow-orange crystals, mp 178–179 °C. The IR spectrum had a band at 1530 cm^{-1}, but no bands between 1550 and 2200 cm^{-1}. ^1H NMR spectrum: δ 8.11 (q, 4 H), 6.43 (s, 1 H), 3.19 (s, 6 H), 1.50–2.90 (complex, 8 H). Anal. ($C_{10}H_{19}N_3O_5S$) C, H, N, S.

C. With Tosyl Azide and Methanol. A solution of 1.0 g of **19** in 20 mL of tetrahydrofuran was cooled to −70 °C and 1.2 g of tosyl azide was added. The solution was allowed to warm until bubbles of gas began to form, and then was cooled to −70 °C again. After the addition of 10 mL of dry methanol, the solution was allowed to warm to room temperature and was stirred for 20 h. Removal of the solvent and chromatographic separation of the residue gave 1.0 g of *N,N*-dimethyl-*p*-toluenesulfonylformamidine. Further elution of the column gave 0.5 g of a material which appeared to be a 1:1 adduct of the enamino ketone and tosyl azide, less the elements of nitrogen, in analogy with the results described under B above. No other material could be isolated.

D. With Polymeric Arylsulfonyl Azide and Methanol. The polymeric azide was prepared with a calculated activity of 4.7 mequiv/g.[20] A solution of 1.5 g of **19** in 20 mL of dichloromethane was cooled to −70 °C and 6.0 g of the polymeric azide was added. The stirred solution was allowed to warm until bubbles of gas started to form, and then was cooled to −70 °C again. About 10 mL of dry methanol was added, and the solution was allowed to warm to room temperature and was stirred for 20 h. The solution was decanted and carefully concentrated. Analysis of the residue by GC (4-ft 30% SE-30, 120 °C) showed two main components with 6.8 and 11.5 min retention times in a 3:1 ratio. Separation was effected by preparative GC. The first component was shown to be methyl 2-cyclopentene-2-acetate by comparison with an authentic sample.[25] The second was found to have an IR carbonyl band at 1745 cm^{-1}, ^1H NMR bands at δ 3.22 (s, 3 H), 2.98 (d, 2 H), 1.8–2.9 (complex, 9 H), and MS molecular ion at *m/e* 140. Anal. ($C_8H_{12}O_2$) C, H. These data indicate the structure to be 2-methoxy-*trans*-bicyclo[3.2.0]heptane (**22**).

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References and Notes

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(25) Prepared by the esterification of 2-cyclopentene-1-acetic acid (Aldrich Chemical Co.).

Stereochemistry of Nucleophilic Solvent Participation in the Decomposition of Diacyl Peroxides

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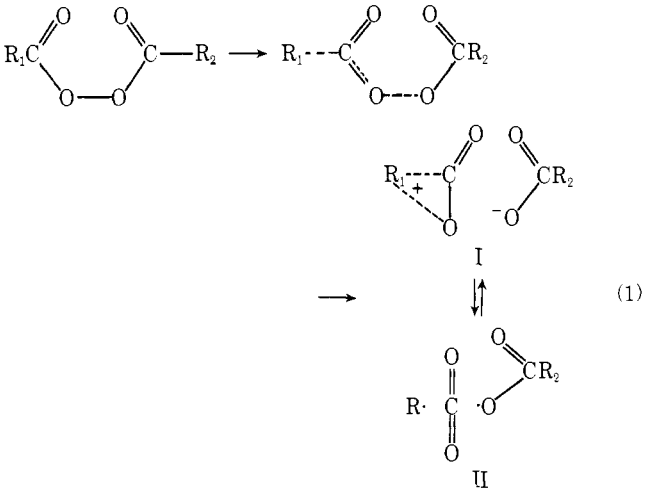
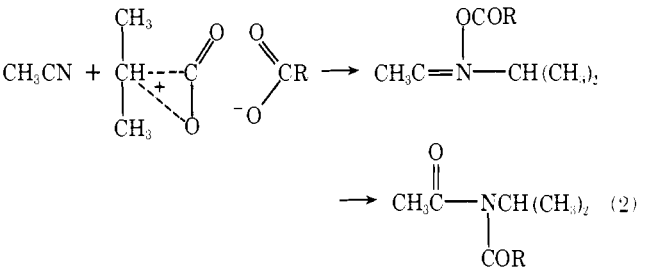
Abstract: Decomposition of (*S*)-(+)-*m*-chlorobenzoyl 2-methylbutanoyl peroxide in acetonitrile yields, among other products, *N*-acetyl-*N*-*m*-chlorobenzoyl-2-butylamine with 14.4% net inversion of configuration. Similar nucleophilic participation is observed in acetic acid and 2-butanol to yield 2-butyl acetate (14% net inversion) and di-2-butyl ether. In these solvents and in cyclohexane and CCl_4, carboxyl inversion product (*m*-chlorobenzoyl-2-butylcarbonate), on the other hand, is formed with retention of configuration. Decomposition of *cis*- and *trans*-4-*tert*-butylcyclohexylformyl *m*-chlorobenzoyl peroxide gives somewhat more complex stereochemical results, but again products involving solvent capture in acetonitrile, acetic acid, and 2-butanol show largely loss of original stereochemistry. Chemically induced dynamic nuclear polarization experiments with several peroxides show no evidence of polarization in any carbonyl-containing products. These results are discussed on the basis of a single rate-determining step in the polar and radical decompositions of diacyl peroxides and the lifetimes of intermediate ion radical pairs.

It is well established that the rapid decomposition of diacyl peroxides $R_1COO\text{-}OCOR_2$, in which one or both R's are secondary or tertiary alkyl, or a resonance stabilized fragment such as benzyl, involves a concerted scission of at least two bonds.[1] Further, decomposition rates are quite solvent dependent, increasing with solvent polarity, yields of scavengeable radicals are often very low, and both "radical" and "polar" products are produced, the best characterized of the latter being the carboxyl inversion product $R_1OCO\text{-}OCOR_2$. This dichotomy has often been discussed as arising from competing discrete radical and ionic decomposition paths, but, in 1970, we proposed[2] that all products could, as well, arise from a common rate-determining transition state, with partitioning into radical and ion pairs occurring at a later stage, with I going on to ionic products, and II either recombining (after



(1)

possible loss of another CO_2) or escaping from the solvent cage to yield scavengeable radicals. Whether I and II should be regarded as species in equilibrium or contributing resonance structures to a common species was not clear and is considered further in this paper. Although this interpretation has been frequently cited and has received some acceptance,[1] only a few[3] additional data have appeared which bear on its validity. An interesting feature of these decompositions is that, in acetonitrile, the solvent is able to capture the ion pair structure I,



(2)

to yield a mono- or diacylamine, sometimes as a major product,[2,3] e.g., with isobutyryl *m*-chlorobenzoyl peroxide (R = *m*-chlorophenyl). It is well established that, in a number of cases, the carboxyl inversion process gives a product, $R_1OCO\text{-}OCOR_2$ with clean retention of configuration at R_1.[1] It occurred to us that an investigation of the stereochemistry of products arising from acetonitrile trapping might give further insight into the nature and lifetime of the ion pair structure (I) and indicate how early in the decomposition process nucleophilic participation by acetonitrile becomes important.

This paper describes the result of our study, and also shows that other nucleophilic solvents are able to trap the ion pair (I).

Results

***m*-Chlorobenzoyl 2-methylbutanoyl peroxide** was chosen for most of our work because of its structural similarity to *m*-chlorobenzoyl isobutyryl peroxide which we had investigated previously and had shown to give good yields of diacylisopropylamine in acetonitrile.[2] The (*S*)-(+) enantiomer was prepared from (*S*)-(−)-2-methyl-1-butanol by oxidation of 2-methylbutanoic acid, conversion to the acid chloride, and re-

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