that of the betaine **5**,[9] and thus the former give stable ylides and the latter gives a betaine.

Possibly the high acidity of the betaine in the case of the ylide **1b** is due to a resonance effect of the phenyl group.

Experimental Section

Materials.—Benzoyl isocyanate was prepared according to the procedure of Speziale:[10] bp 99–101° (20 mm); ir 2240 cm^{-1} (NCO).

The ylides **1a**,[11] **4a**,[12] and **4b**[12] were prepared according to the known procedures. The physical properties were identical with reported data.

Reaction of the Ylide 1a.—Benzoyl isocyanate (0.02 mol) dissolved in 3 ml of benzene was added dropwise to 0.02 mol of the ylide **1a** dissolved in 200 ml of benzene under a nitrogen stream. The mixture was stirred at 50° for 3 hr. The resulting precipitate was filtered off and recrystallized with methanol to give 6.0 g (93%) of the ylide **2a**: mp 195–196.5°; ir (Nujol) 3200 (NH), 1700, 1640, 1600 cm^{-1} (CO); nmr (CDCl$_3$) δ 0.52 (t, 3, $J = 7.1$ Hz, CH$_3$), 3.73 (q, 2, $J = 7.1$ Hz, CH$_2$), 12.62 (s, 1, NH); mol wt (vpo, CHCl$_3$) 498 (calcd 496).

Anal. Calcd for $C_{30}H_{26}O_4NP$: C, 72.72; H, 5.29; N, 2.83. Found: C, 72.95; H, 5.35; N, 2.86.

Hydrolysis of the Ylide 2a.—The ylide **2a** (1.5 g) was dissolved in 50 ml of EtOH, and a small quantity of NaOH was added. The mixture was refluxed for 10 hr, concentrated, extracted (benzene), and recrystallized (MeOH) to give 0.7 g (60%) of the ylide **3a**: mp 192–193°; ir (CHCl$_3$) 3560, 3360 (NH), 1620, 1600 cm^{-1} (CO); nmr (CDCl$_3$) δ 0.52 (t, 3, $J = 7.5$ Hz, CH$_3$), 3.69 (q, 2, $J = 7.5$ Hz, CH$_2$); mass spectrum (70 eV) m/e 391 (M$^+$, calcd 391), 347 ($Ph_3P{=}CCOOEt^+$), 319 ($Ph_3P{=}CHCOO^+$).

Anal. Calcd for $C_{23}H_{22}O_3NP$: C, 70.58; H, 5.66; N, 3.58. Found: C, 70.92; H, 5.81; N, 3.49.

Reaction of the Ylide 1b.—The mixture of 0.04 mol of phenyllithium, 0.03 mol of benzyltriphenylphosphonium chloride, and 150 ml of ether was stirred for 8 hr at room temperature under a nitrogen stream.[13] Benzoyl isocyanate (0.03 mol) was added dropwise, and stirring was continued for 7 hr. The reaction mixture was concentrated and recrystallized (benzene–methanol) to give 15.0 g (73%) of the ylide **2b**: mp 176.5–178°; ir (CHCl$_3$) 3440 (NH), 1690, 1610 cm^{-1} (CO); nmr (CDCl$_3$) δ 8.12 (b, NH, disappeared by D$_2$O addition); mass spectrum (70 eV) m/e 499 (M$^+$, calcd 499), 379 ($Ph_3P{=}C(Ph)CO^+$), 351 ($Ph_3P{=}CPh^+$).

Anal. Calcd for $C_{33}H_{26}O_2NP$: C, 79.34; H, 5.25; N, 2.80. Found: C, 79.69; H, 5.24; N, 2.64.

Reaction of the Ylide 4a.—Benzoyl isocyanate (0.02 mol) was added dropwise to 0.02 mol of the ylide **4a** dissolved in 100 ml of toluene, and the mixture was stirred for 3 hr at 60° under a nitrogen stream. The resulting precipitate was recrystallized (MeOH–Et$_2$O) to give 9.5 g (90%) of the betaine **5a**: mp 169–170°; ir (CHCl$_3$) 1700, 1640, 1580 cm^{-1} (CO); nmr (CDCl$_3$) δ 1.68 (s, 1, CH); mass spectrum (70 eV) m/e 380 ($Ph_3P{=}CHCOPh^+$), 147 ($PhCONCO^+$).

Anal. Calcd for $C_{34}H_{26}O_3NP$: C, 77.41; H, 4.98; N, 2.67. Found: C, 77.12; H, 4.92; N, 2.65.

Decomposition of the Betaine 5a. A.—The betaine **5a** (2.5 g) was heated at 180° for 15 min under reduced pressure (20 mm). Benzoyl isocyanate was trapped as benzamide. The residue was chromatographed (Al$_2$O$_3$, benzene) to give 1.55 g (86%) of the ylide **4a**.

B.—The ethanol solution of the betaine **5a** was refluxed for 7 hr in the presence of a small quantity of HBr. The ylide **4a** was recovered quantitatively.

Reaction of the Ylide 4b.—The ylide **4b** reacted with benzoyl isocyanate in the same manner as the ylide **4a** to give the betaine **5b**: yield 85%; mp 196.5–197.5° (recrystallized from MeOH–Et$_2$O); ir (Nujol) 1700, 1620, 1540 cm^{-1} (CO); mass spectrum (70 eV) m/e 318 ($Ph_3P{=}CHCOMe^+$), 147 ($PhCONCO^+$).

Anal. Calcd for $C_{29}H_{24}O_3NP$: C, 74.83; H, 5.20; N, 3.01. Found: C, 74.58; H, 4.94; N, 3.01.

Decomposition of the Betaine 5b.—The ethanol solution of the betaine **5b** was refluxed for 8 hr in the presence of a small quantity of NaOH. The ylide **4b** was recovered quantitatively by extraction with benzene.

Reaction of the Ylide 6.—The mixture of 0.01 mol of methyltriphenylphosphonium bromide, 0.01 mol of NaH, and 200 ml of THF was stirred for 8 hr.[14] After separation of the insoluble solid, 0.02 mol of benzoyl isocyanate was added dropwise, and stirring was continued for 7 hr at room temperature under a nitrogen stream. The reaction mixture was concentrated and extracted (benzene). Insoluble solid was recrystallized (MeOH–benzene) to give 2.2 g (43%) of the ylide **9**: mp 282–283°; ir (Nujol) 3420 (NH), 1750, 1700, 1640, 1600 cm^{-1} (CO); mass spectrum (70 eV) m/e 492 (M$^+$, calcd 492), 449 (M$^+$ − HNCO), 431 (M$^+$ − CONHCO), 147 ($PhCONCO^+$).

Anal. Calcd for $C_{29}H_{21}O_4N_2P$: C, 70.53; H, 4.30; N, 5.69. Found: C, 70.52; H, 4.26; N, 5.61.

The extract with benzene was recrystallized (benzene–hexane) to give 0.5 g (19%) of the triazine **10**: mp 239–240°; ir (Nujol) 1520 cm^{-1}, identical with that of the authentic sample;[15] mass spectrum (70 eV) m/e 309 (M$^+$, calcd 309).

Anal. Calcd for $C_{21}H_{15}N_3$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.50; H, 4.59; N, 13.56.

Registry No.—**2a**, 29411-29-8; **2b**, 29411-30-1; **3a**, 29520-63-6; **5a**, 29411-31-2; **5b**, 29250-64-7; **9**, 29411-32-3; benzoyl isocyanate, 4461-33-0.

Acknowledgment.—The authors thank Mr. Yutaka Ohno for his help in the experiments.

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[10] A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **28**, 1805 (1963).

[11] D. B. Denney and S. T. Ross, *ibid.*, **27**, 998 (1962).

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[13] G. Wittig and M. Rieber, *Justus Liebigs Ann. Chem.*, **562**, 177 (1949); ref 1, p 52.

[14] J. Asunskis and H. Schechter, *J. Org. Chem.*, **33**, 1164 (1968).

[15] S. Yanagida, H. Hayama, M. Yokoe, and S. Komori, *ibid.*, **34**, 4125 (1969).

Spontaneous Ring Enlargement during the Free-Radical Bromination of 2-Benzyl-1,3,3-trimethyl- and 2-Benzyl-3,3-dimethylbicyclo[2.2.1]heptanol-2

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Previous publications[1] have reported a simple method by which one may effect a ring expansion, namely, through the decomposition of the magnesium salts of halohydrins with appropriate structures (eq 1). New examples[1b,d] (eq 2) were cited of the previously reported[2] anomalous migration (in the norbornyl system) of the *less*-substituted C-2–C-3 bond instead of the *more*-substituted C-1–C-2 bond to an incipient electron-deficient center.[3] The latter occurs even though the transition state proceeds through the less favorable boat conformation (eq 2) in preference to the chair conformation. It is apparent that one must consider some factor(s) opposing both electronic and boat form interactions in the transition state. Sauers[2] offered a rationale by proposing a third factor. The factor is

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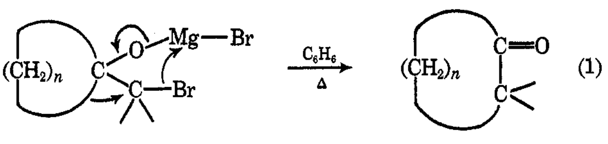
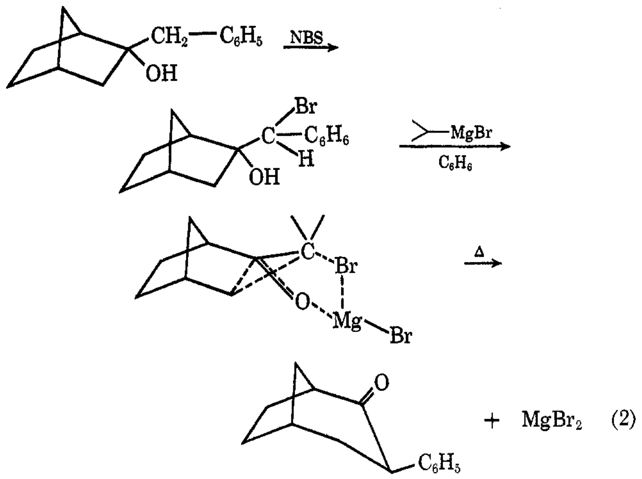
[1] A. J. Sisti, *J. Org. Chem.*, **33**, 453 (1968); (b) A. J. Sisti, *Tetrahedron Lett.*, No. 52, 5327 (1967); (c) A. J. Sisti, *J. Org. Chem.*, **33**, 3953 (1968); (d) A. J. Sisti, *ibid.*, **35**, 2670 (1970).

[2] R. R. Sauers and J. A. Beisler, *ibid.*, **29**, 210 (1964).

[3] Only the Baeyer–Villiger reaction of norbornanone-2 (migration to oxygen) is exceptional in that it alone is controlled by electronic factors (C-1–C-2 bond migration). J. A. Berson and S. Suzuki, *J. Amer. Chem. Soc.*, **81**, 4088 (1959), have concluded that migrations to oxygen should be most sensitive to electrical changes in the migrating groups.

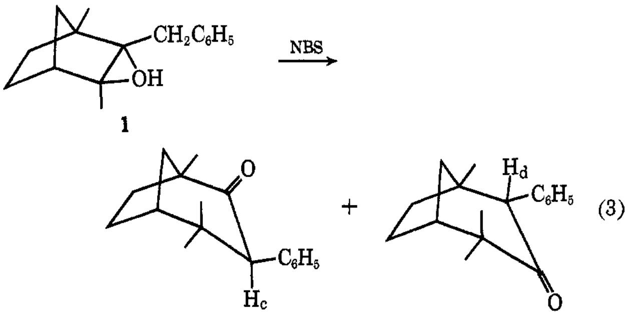


$n = 4, 5, 6$, and 7



associated with the torsional strain resulting from the eclipsed nonbonded interactions between the substituents on C-2 and the hydrogens on C-3. Nonbonded interactions between the groups on C-2 and the bridgehead substituent are much less since the dihedral angles are 44 and 79°. Therefore, C-2–C-3 bond migration entails much more relief of eclipsing strain than C-1–C-2 bond migration.

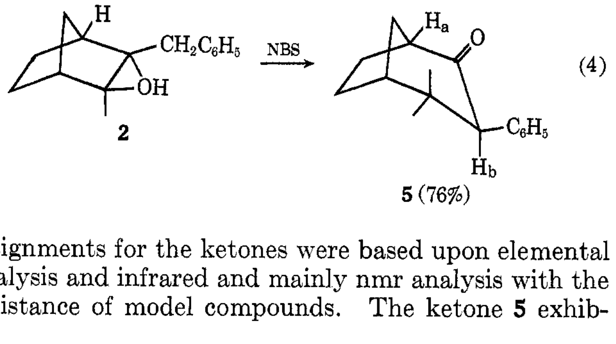
Reported herein are two unusual examples which further substantiate the Sauers' postulate. When 2-benzyl-1,3,3-trimethylbicyclo[2.2.1]heptanol-2 (**1**) and 2-benzyl-3,3-dimethylbicyclo[2.2.1]heptanol-2[4] (**2**) were treated with *N*-bromosuccinimide and benzoyl peroxide in refluxing carbon tetrachloride, a spontaneous ring enlargement transpired (eq 3 and 4). The structural assignments for the ketones were based upon elemental analysis and infrared and mainly nmr analysis with the assistance of model compounds. The ketone **5** exhibited the following nmr signals: multiplet at τ 7.1–7.3 assigned to the bridgehead hydrogen α to a carbonyl group (H_a), a singlet at τ 6.60 ascribed to the benzyl hydrogen α to a carbonyl group (H_b) (migration of the C-1–C-2 bond in **2** would have resulted in the production of 4,4-dimethyl-2-phenylbicyclo[3.2.1]octanone-3 and not **5**; the former would have produced a doublet for the benzyl hydrogen α to a carbonyl group[5]), and signals for the methyl groups at τ 9.07 and 9.15. The model compounds employed for comparison were norbornanone-2, bicyclo[3.2.1]octanone-2, 3-methylbicyclo[3.2.1]octanone-2,[1d] and 3-phenylbicyclo[3.2.1]octanone-2[1b] with the bridgehead hydrogen α to the carbonyl group (all multiplets similar to H_a in **5**) at τ 7.30, 7.30, 7.35, and 7.25, respectively. The ketone **3** gave signals at τ 6.68 (benzyl hydrogen α to a carbonyl group H_c) and for the methyl groups at τ 8.89, 9.10, and 9.20. The product **4** exhibited signals at τ 6.45 (benzyl hydrogen α to a carbonyl group H_d) and the methyl groups at τ 9.18, 8.94, and 8.78. The τ values lower than 9, in each case, were attributed to the methyl groups on a carbon α to the carbonyl group. The model compounds from which the structural assignments were made were 3-methylbicyclo[3.2.1]octanone-2[1d] and **5**. The stereochemical assignment for the phenyl group assumes the more stable conformation as given in **3**, **4**, and **5**. The basis for the assignment was twofold: previous equilibration studies with 3-phenylbicyclo[3.2.1]octanone-2[1b] and an equilibration study with **3** in trifluoroacetic acid.



1

3 (48%)

4 (7%)

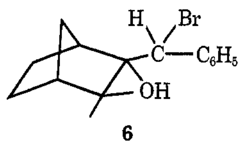


2

5 (76%)

The presence of the methyl groups (C-3, **1** and **2**) raises the magnitude of the unfavorable nonbonded interactions between the eclipsed groups on C-2 and C-3 resulting in an increase in the torsional strain (compared to the bromohydrin in eq 2 which is stable under the same preparative conditions). Thus, the release of strain supplies the driving force for the spontaneous decomposition (eq 3) during the free-radical bromination. It should also be noted that each compound, **1** and **2**, decomposes to the ring-enlarged ketones **3** and **5** as a result of the highly preferential migration of the C-2–C-3 bond over the C-1–C-2 bond. Particularly noteworthy is the result from the fenchone system, **1**, which apparently further substantiates the Sauers' postulate. The electronic effects are essentially equal, and competition is between proceeding through the more favorable chair form (migration of C-1–C-2 bond) *vs.* the less favorable boat form involving the release of torsional strain (migration of C-2–C-3 bond); the latter consideration predicts the observed major product, **3**, over **4**.

The possibility that the conversion of **1** and **2** to the ring-enlarged ketones (eq 3) might have involved an alkyl migration (C-2–C-3 bond) to a free-radical center was dampened by subsequent experimentation. The bromohydrin **6** was shown to be a reasonable inter-



6

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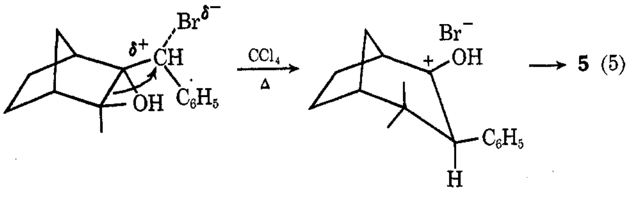
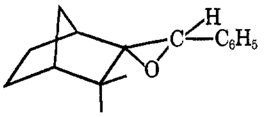
[4] Precedent argues that the stereochemical assignments of these alcohols is as presented in **1** and **2**, *exo*-2-benzyl groups and *endo*-2-ols (see ref 2).

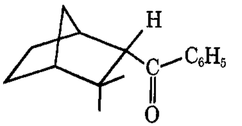
[5] The doublet is expected from inspection of models; however, tangible support is offered from the nmr spectra of 2-phenyl-3-methylcyclohexanone and 2-phenyl-3-methylcycloheptanone doublets at τ 6.94 and 6.77, respectively (unpublished results).

mediate during the conversion of **2** to **5** (eq 4) by its synthesis from **2** with bromine in carbon tetrachloride (light catalyzed) at room temperature followed by its decomposition in refluxing carbon tetrachloride to **5**. In addition, treatment of **2** in carbon tetrachloride with benzoyl peroxide gave no evidence of any products resulting from migration of an alkyl group to a free-radical center. The latter, coupled with the known reluctance of an alkyl group to migrate to a free-radical center,[6] leads one to an ionic interpretation for the production of the ring-enlarged ketones (eq 5). Lastly, a mechanism *via* an epoxide intermediate **7** was ruled out since none of the expected carbonyl compounds therefrom, **8** and **9**, were detected.





7



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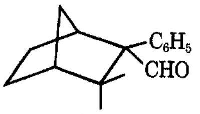

9

Experimental Section[7]

2-Benzyl-1,3,3-trimethylbicyclo[2.2.1]heptanol-2 (1) and 2-Benzyl-3,3-dimethylbicyclo[2.2.1]heptanol-2 (2) were prepared by the dropwise additions of 80-ml ether solutions of fenchone and camphenilone (0.35 mol), respectively, into benzylmagnesium chloride (from 53 g of benzyl chloride, 11.4 g of magnesium, and 300 ml of ether). After the addition the solution was refluxed for 14 and 24 hr, respectively, and then decomposed (NH_4Cl). The separated organic portion was washed with water and dried ($MgSO_4$). After removal of the solvent under vacuum the alcohol **1** was distilled yielding 72 g (0.30 mol) (87%) of a liquid, bp 112–116° (0.2 mm). The alcohol was crystallized from aqueous ethanol after 1 month in the refrigerator: mp 57–59°; vpc (10% Carbowax on Chromosorb W, 142°, 40 psi) showed one peak; ir spectrum (CCl_4) 3590 cm^{-1} (OH); nmr (CCl_4) τ 7.23 (s, benzyl hydrogens).

Anal. Calcd for $C_{17}H_{24}O$: C, 83.55; H, 9.90. Found: C, 83.63; H, 9.94.

The alcohol **2** was crystallized and recrystallized from methanol yielding 71 g (0.30 mol) (89%), mp 45–47°. After three recrystallizations followed by vacuum drying (24 hr), it had mp 48–49.5°; ir spectrum (CCl_4) 3585 cm^{-1} (OH); nmr (CCl_4) τ 7.26 (s, benzyl hydrogens).

Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.51; H, 9.72.

4,4-Dimethyl-3-phenylbicyclo[3.2.1]octanone-2 (5).—A mixture of 5.75 g (0.025 mol) of **2**, 4.8 g (0.027 mol) of *N*-bromosuccinimide, 75 ml of carbon tetrachloride, and 0.1 g of benzyl peroxide was refluxed for 2 hr. The mixture was then cooled and filtered and the filtrate was washed successively with water, 10% sodium carbonate, and water and dried ($MgSO_4$). The solvent was removed under vacuum and the residual solid was recrystallized from carbon tetrachloride yielding 4.3 g (0.190 mol) (76%) of a white solid **5**: mp 139–140°; ir spectrum ($CHCl_3$) 1705 cm^{-1} (C=O); nmr (CCl_4) τ 6.60 (s, benzyl hydrogen α to a carbonyl group), 7.10–7.30 (m, bridgehead hydrogen α to a carbonyl group), 9.07 and 9.15 (s, two methyl groups on carbon α to a phenyl group).

Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 83.97; H, 8.67.

2-(α-Bromobenzyl)-3,3-dimethylbicyclo[2.2.1]heptanol-2 (6).—Into a 100-ml three-necked round-bottom flask was placed 42 ml of carbon tetrachloride and 5.75 g (0.025 mol) of **2**. The flask was fitted with a thermometer, dropping funnel, and condenser (maintained nitrogen sweep during the entire reaction). Bromine, 4.0 g (0.025 mol), in 8 ml of carbon tetrachloride was added dropwise over a 2.5-hr period during which time the flask was irradiated (Sperti P106 uv lamp) and the temperature kept below 28°. The solution was then washed with water and 10% sodium carbonate and dried ($MgSO_4$). The solvent was removed from one-third of the solution yielding 2.13 g of a light yellow oil: positive silver nitrate; ir spectrum (film) 3550 cm^{-1} (OH); nmr (CCl_4) τ 4.70 (s, benzyl hydrogen).

The remaining solution was refluxed for 2 hr and then washed with 10% sodium carbonate and water and dried ($MgSO_4$). After removal of the solvent and three recrystallizations from pentane, there was obtained the ketone **5**: 1.39 g (0.0061 mol) (38%); mp 141–142°; mixture melting point showed no depression; ir spectrum identical with that of **5**.

Reaction of 2-Benzyl-1,3,3-trimethylbicyclo[2.2.1]heptanol-2 (1) with *N*-Bromosuccinimide.—Into a flask was placed 12.2 g (0.050 mol) of **1**, 9.5 g (0.055 mol) of *N*-bromosuccinimide, 0.2 g of benzoyl peroxide, and 125 ml of carbon tetrachloride. The mixture was brought to reflux, at which time an extremely vigorous reaction occurred after which the mixture was refluxed for an additional 0.5 hr. The mixture was then cooled and filtered and the solvent removed under vacuum. Distillation of the residue yielded 8.15 g of product, bp 121–124° (0.10 mm), the nmr of which indicated a mixture of several components, primarily, 1,4,4-trimethyl-3-phenylbicyclo[3.2.1]octanone-2 (**3**) (48% based on **1**) and a minor (5–10%) amount of 1,4,4-trimethyl-2-phenylbicyclo[3.2.1]octanone-3 (**4**) (yields based upon ratio of integrations of the benzyl hydrogens to the total integration of the phenyl hydrogens).

An aliquot (1.0 g) of the distillate was crystallized with pentane (7 ml) yielding *pure* **3**: mp 49–51.5°; 0.48 g (30% based on **1**); ir spectrum (CCl_4) 1710 cm^{-1} (C=O); nmr (CCl_4) τ 2.90–3.20 (m, phenyl hydrogens), 6.68 (s, benzyl hydrogen α to a carbonyl group), 8.89 (s, bridgehead methyl group on carbon α to a carbonyl group), 9.10 and 9.20 (s, methyl groups on carbon α to a phenyl group).

Anal. Calcd for $C_{17}H_{22}O$: C, 84.20; H, 9.15. Found: C, 84.20; H, 9.20.

The 2,4-dinitrophenylhydrazone had mp 161.5–162.5° (EtOH).

Anal. Calcd for $C_{23}H_{26}N_4O_4$: C, 65.39; H, 6.20; N, 13.26. Found: C, 65.28; H, 6.16 N, 13.39.

The nmr analysis of the previous filtrate revealed that an additional 0.2 g of **3** was present [total **3**, 0.69 g (46% based upon **1**)].

An aliquot (2.0 g) of the original distillate was now chromatographed (100 g of Woelm acid washed alumina, grade I) with the following results. Elution with 150 ml of hexane gave a pure sample of 2-benzylidene-1,3,3-trimethylbicyclo[2.2.1]heptane (dehydration product from **1**), 0.24 g (12% based on **1**). The structural assignment was based upon ir spectrum (film) 1663 cm^{-1}; nmr (CCl_4) τ 3.88 (s, vinyl hydrogen). Final elution (200 ml of benzene followed by 400 ml of chloroform) gave a mixture of **3** and **4** which resisted separation. Examination of the nmr (CCl_4) revealed the presence of the ketone **4**: nmr τ 6.45 (s, benzyl hydrogen α to a carbonyl group), 8.78 and 8.94 (s, methyl groups on a carbon α to a carbonyl group), 9.18 (s, bridgehead methyl on a carbon α to a phenyl group). Based upon the integration of the benzyl hydrogen in **4** relative to the benzyl hydrogen in **3** and to the total phenyl hydrogens in the sample, it was estimated that **4** represented 10% of the sample (7% based on **1**). The ketone **3** represented 70% of this sample (47% based on **1**).

Reaction of 2-Benzyl-3,3-dimethylbicyclo[2.2.1]heptanol-2 (2) with Benzoyl Peroxide.—Into a flask was placed 2.30 g (0.01 mol) of **2**, 2.42 g (0.01 mol) of benzoyl peroxide, and 25 ml of carbon tetrachloride. The mixture was refluxed for 24 hr followed by removal of the solvent under vacuum. The residue was dissolved in pentane and washed with a 10% solution of sodium

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[6] C. Walling in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 407.

[7] All melting points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Spectracord infrared spectrophotometer. The nmr spectra were determined with a Varian A-60 instrument.

carbonate. The solvent was removed under vacuum and gave no evidence of the presence of ketone **5** as confirmed by the ir spectrum (no C=O absorption at 1705 cm^{-1}), and nmr (CCl_4) showed no benzyl hydrogen at τ 6.60.

Registry No.—**1**, 29478-03-3; **2**, 29478-04-4; **3**, 29478-05-5; **3** 2,4-DNP, 29478-06-6; **5**, 29478-07-7; **6**, 29478-08-8; *N*-bromosuccinimide, 128-08-5.

Halogenated Ketenes. XX. Substitution *vs.* Rearrangement of Halogenated Ketene Olefin Cycloadducts[1,2]

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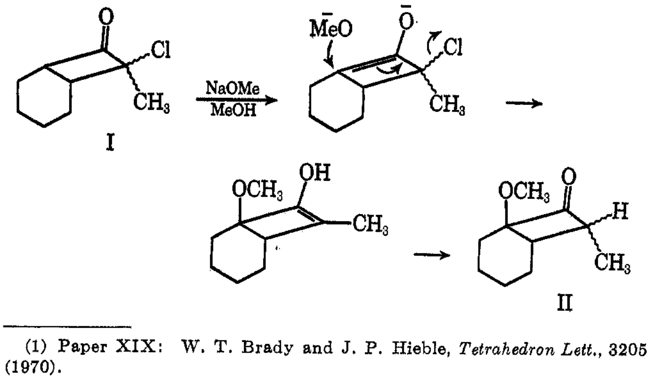
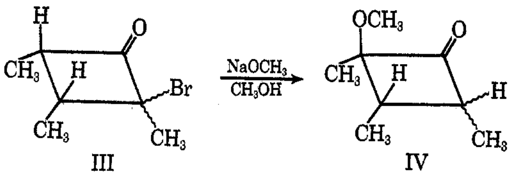
Received November 4, 1970

Two communications have recently appeared which describe a base-catalyzed rearrangement of a cycloadduct of a halogenated ketene and an olefin leading to a bifunctional cyclopropane.[3,4] These reports prompt us to describe our results on the rearrangement of a bicyclo[3.2.0]hept-2-en-6-one ring system to the bicyclo[3.1.0]hex-2-ene ring system in the presence of sodium methoxide in refluxing methanol. This ring system undergoes rearrangement in contrast to other systems studied by us and other workers which undergo substitution under similar conditions.

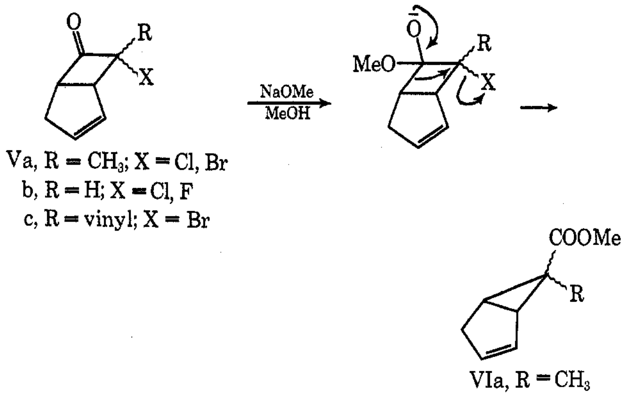
Fletcher and Hassner have reported that the dichloroketene adducts of cholestene and cyclohexene undergo rearrangement under the influence of methoxide to produce 1-methoxy-7-carbomethoxybicyclo[4.1.0]heptane in the latter case and the corresponding rearranged product in the former. A proposed mechanism involves enolization, followed by methoxy substitution on C_6 (this intermediate was isolated) and subsequent loss of the second chlorine atom and rearrangement to the bicyclo[4.1.0]heptane derivative.

When the adduct of methylchloroketene and cyclohexene (I) was treated with a threefold excess of sodium methoxide in refluxing methanol, II was obtained in approximately 60% yield as the only volatile product. This compound corresponds to Hassner's intermediate, except that in this case a second leaving group is not available for further rearrangement. Similarly, when the adduct of methylbromoketene and *cis*-2-butene (III) was treated with methoxide, the substitution product (IV) was obtained in 70% yield.





However, when the methylchloro- or methylbromoketene adduct of cyclopentadiene (V) was heated with sodium methoxide in methanol, rearrangement occurred rather than substitution. The methoxide ion attacks the carbonyl carbon atom, thus leading to the rearranged product (VI). This is consistent with the mechanism proposed by Brook, *et al.*, and is formally analogous to the Favorski rearrangement of α-haloketones.[4,5] This rearrangement was observed with several halogenated ketene–cyclopentadiene adducts as illustrated.

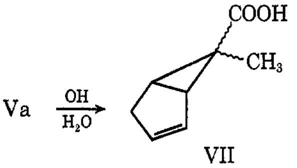


Va, R = CH_3; X = Cl, Br
b, R = H; X = Cl, F
c, R = vinyl; X = Br

VIa, R = CH_3
b, R = H
c, R = vinyl

The structure of VI was established by elemental analysis, infrared spectra and the following nmr and and mass spectral data. The chemical shift of the bridgehead protons in the nmr spectra of VI ranged from δ 1.0 to 2.5, and the corresponding bridgehead protons in the bicyclo[3.2.0]hept-2-en-6-ones appear at δ 3.5–4.3;[6] the chemical shift of the ester methoxy protons occurred at a position characteristic of an ester (δ 3.5–3.7) rather than at a position characteristic of an ether (δ 3.2–3.3). A parent peak at *m/e* 152 for VIa was observed in the mass spectrum; a very intense peak was also observed at *m/e* 93 resulting from the loss of a carbomethoxy group.

As a further verification of the structure of VIa, Va was treated with 20% aqueous sodium hydroxide solution, resulting in the formation of a carboxylic acid (VII). This acid was converted to the methyl ester by treatment with thionyl chloride and then methanol.



VII

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(1) Paper XIX: W. T. Brady and J. P. Hieble, *Tetrahedron Lett.*, 3205 (1970).

(2) Support of this investigation by The Robert A. Welch Foundation, National Science Foundation (GP-14016), and a North Texas State University Faculty Research Grant is gratefully acknowledged.

(3) V. R. Fletcher and A. Hassner, *ibid.*, 1071 (1970).

(4) P. R. Brook, J. M. Harrison, and A. J. Duke, *Chem. Commun.*, 589 (1970).

(5) A. S. Kende, *Org. React.*, **11**, 261 (1960).

(6) W. T. Brady and R. Roe, Jr., *J. Amer. Chem. Soc.*, **92**, 4618 (1970).