for the formation of acidic products was obtained by isolation of the acid and the determination of its melting point. Thus, benzoic acid (m.p. 122°), *p*-nitrobenzoic acid (m.p. 243°), *o*-toluic acid (m.p. 180°), and phthalic acid (206–7°) were further substantiated. Coupling products were also formed from *p*-nitrotoluene but no attempt to obtain quantitative data on them was made.

Dielectric Measurements.—All dielectric measurements on molten DPSO were obtained with Sargent oscillometer between 78 and 110; all pertinent data are summarized in Table VI.

Table VI

Determination of Dielectric Constant (ϵ) of DPSO

ϵ	Temp., °C.	Oscillometer ± 150
15.0	110	10,557
15.8	100	10,612
16.0	97	10,916
16.4	91	11,035
16.8	84	11,183
17.0	78	11,326

Carbon–Carbon Bond Fission in Cyclopropanes. V. The Acid-Promoted Opening of the Three-Membered Ring in Bicyclo[5.1.0]octane

Robert T. LaLonde and LeRoy S. Forney[1]

Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse, New York 13210

Received April 24, 1964

The acid-promoted opening of bicyclo[5.1.0]octane gives 1-methylcycloheptene as the predominant olefin and a mixture of acetates which largely consists of *cis*- and *trans*-2-methylcycloheptyl acetate. The *trans* isomer is found only in slight excess of the *cis* isomer. The reactivity and extent of transannular hydride shift in the ring opening of some bicyclo[n.1.0]alkanes and epoxycycloalkanes are compared. Mechanistic implications of the results are discussed.

The acetate formation accompanying the acid-promoted opening of strained bonds in some bicyclo[*n*.1.0]alkanes[2] was found to be largely, though not completely, stereoselective. This result has been attributed to an S$_N$2 nucleophilic solvent attack on a protonated[3] three-membered ring prevailing over a competing carbonium ion pathway. However, S$_N$2 displacements in seven-membered and medium-sized rings, relative to aliphatic substrates, are subject to a rate retardation[4-6] attributed to the sterically induced noncollinearity of the leaving group and nucleophile.[7] These results and their interpretation suggested that a higher activation energy would possibly be involved in a nucleophilic solvent attack of a protonated, strained carbon–carbon bond in bicyclo[5.1.0]octane[8] than in the bicyclo[*n*.1.0]alkanes studied previously. Consequent to this higher activation energy would be the compression of transition state energies of nucleophilic solvent attack and carbonium ion processes. The anticipated, observable result would be a loss of stereoselectivity in the formation of acetate from bicyclo[5.1.0]octane.

In continuation of our studies of the acid-promoted opening of the three-membered ring in bicyclo[*n*.1.0]alkanes we carried out an analysis of the products arising from bicyclo[5.1.0]octane when it was treated with 0.07 *N* sulfuric acid in glacial acetic acid. The product mixture obtained from a 47-hr. reaction was shown by gas chromatography to contain 40% olefin and 60% acetate. Further analysis of the product mixture demonstrated the presence of 1-methylcycloheptene (79%), 3-methylcycloheptene (15%), vinylcyclohexane (4%), cyclooctene (1%), and unconverted bicyclo[5.1.0]octane (<1%). Identification of the olefins was made through gas chromatographic retention times obtained from three different columns. The olefins present in 79 and 15% were isolated by gas chromatography and their infrared spectra confirmed their identity with 1-methylcycloheptene and 3-methylcycloheptene, respectively. The presence of 1-ethylcyclohexene, ethylidenecyclohexane, and 4- and 5-methylcycloheptene, all of which were considered possible olefinic reaction products, could not be detected in the olefin component.

After olefin analysis, the crude product mixture was treated with lithium aluminum hydride and the resulting mixture of alcohols was analyzed by gas chromatography in order to ascertain the identity and distribution of acetates in the acetate component (60%). A chromatogram obtained by employing a Castorwax column revealed that the alcohol mixture consisted of mostly (86%) 2-, 3-, and 4-methylcycloheptanols and small amounts of 1-methylcycloheptanol (4%), methylcyclohexylcarbinol (8%), and cyclooctanol (2%). A second chromatogram obtained by employing a glycerol column showed five peaks. Because the resolution of peaks was poor (see Experimental) only a rough determination of relative amounts of each component of the alcohol mixture was possible. One of two major peaks accounted for about 40% of the mixture and had a retention time identical with the retention times of 1-methylcycloheptanol, methylcyclohexylcarbinol, and *cis*-2-methylcycloheptanol. Since chromatography on Castorwax demonstrated that the sum of 1-methylcycloheptanol and methylcyclohexylcarbinol was 12%, the relative amount of *cis*-2-methylcycloheptanol in the alcohol mixture could be set at about 30%. The second major peak (also ~40%) had a retention time identical with only *trans*-2-methylcycloheptanol. Minor components were *trans*-3-

---

[1] National Science Foundation Cooperative Fellow, 1963–1965.

[2] Paper IV: R. T. LaLonde and M. A. Tobias, *J. Am. Chem. Soc.*, in press, and earlier papers in this series.

[3] In this paper we arbitrarily assume that the nucleophilic solvent attack is subsequent to protonation although protonation concerted with nucleophilic attack appears equally possible.

[4] L. Schotsmans, P. J. C. Fierens, and T. Verlie, *Bull. soc. chim. Belges*, **68**, 580 (1959).

[5] P. J. C. Fierens and P. Verschelden, *ibid.*, **61**, 427, 609 (1952).

[6] S. F. Van Straten, R. V. V. Nicholls, and C. A. Winkler, *Can. J. Chem.*, **29**, 372 (1951).

[7] J. Sicher in "Progress in Stereochemistry," P. B. D. de la Mare and W. Klyne, Ed., Butterworth and Co., Washington, D. C., 1962, pp. 226, 227.

[8] An inspection of a Dreiding model of bicyclo[5.1.0]octane in the more favorable of two possible chair conformations reveals that displacement of a protonated carbon–carbon bond by the backside approach would be hindered by C-3 and -5 hydrogen atoms.

methylcycloheptanol (<5%), *cis*- and/or *trans*-4-methylcycloheptanol (~15%), and cyclooctanol (4%). For the purpose of obtaining a more accurate analysis of major components and also to provide support for the identity of the alcohols, the alcohol mixture was oxidized to a mixture of ketones and the latter was examined chromatographically. Components of the ketone mixture were cyclohexyl methyl ketone (6%), 2-methylcycloheptanone and/or 1-methylcycloheptanol (72%), 4-methylcycloheptanone (12%), and cyclooctanone (2%). A fifth component (4%) remained unidentified. The major component was collected and its infrared spectrum displayed only the bands of 2-methylcycloheptanone and the more intense bands of 1-methylcycloheptanol. The second most abundant component was also isolated and its infrared spectrum was found to be identical with the spectrum of 4-methylcycloheptanone. Since chromatographic analysis of the alcohol mixture employing Castorwax column had demonstrated the presence of 1-methylcycloheptanol in 4%, the relative amount of 2-methylcycloheptanone in the mixture of ketones must be 68%. This value is substantially the same as the sum (~70%) of the relative amounts of *cis*- and *trans*-2-methylcycloheptanol in the mixture of alcohols.

In order to ascertain whether the alcohol distribution represented products which were originating directly from bicyclo[5.1.0]octane, the per cent compositions of alcohol mixtures resulting from reactions of various duration were determined. These per cent compositions are given in Table I and it is seen that for those alcohols analyzed there are small changes in the alcohol distribution over the period of nearly 47 hr. These changes can be attributed either to the isomerization of acetates under ring-opening conditions or, what seems more likely on the basis of the evidence available, the formation of acetate by addition of acetic acid to olefin. That addition to olefin does occur is demonstrated by the change in the olefin to acetate ratio over the period of 46 hr. (Table I). Plotting these ratios against time gives a straight-line plot which when extrapolated to zero time gives a value of 1.25 for the olefin to acetate ratio. Therefore, the change in olefin to acetate ratio represents an increase of about 16% in the relative amount of acetate over the period of 46 hr. The change in acetate (alcohol) distribution possibly is the result of addition of acetic acid to both 3-methylcycloheptene and 1-methylcycloheptene with addition to the latter occurring at a slightly greater rate. A greater increase in the relative amounts of 1-methylcycloheptyl acetate and methylcyclohexylcarbinyl acetate, the latter arising through addition accompanied by rearrangement, could make it appear that the relative amounts of 2-, 3-, and 4-methylcycloheptyl acetates were diminishing although the absolute amount of this group of acetates would in fact increase. That changes in alcohol distribution are due to addition to olefins rather than isomerization of acetates tends to be supported by a chromatographic analysis of an alcohol mixture obtained from a 0.5-hr. reaction. Since this analysis was determined on a glycerol column, small changes in composition would not be revealed. Nevertheless the chromatogram shows that *cis*- and *trans*-2-methylcycloheptanol are present in the same approximate ratio after 0.5 hr. as after 47 hr.

Table I

Per Cent Distribution[a] and Ratio of Products[a] Obtained from the Acid-Promoted Opening of Bicyclo[5.1.0]octane in Acetic Acid at 47°

Reaction time, hr.	Olefin–acetate	1-Methylcycloheptanol[b]	2-, 3-, and 4-methylcycloheptanol	Methylcyclohexylcarbinol	Cyclooctanol
0.5		4	93	2	2
1.0	1.31	4	91	3	2
8	1.09	4	87	7	2
8	0.93	5	88	6	2
21	1.07	6	85	7	2
44	0.75				
47	0.67	4	86	8	2

[a] Determined by vapor phase chomatography. [b] The maximum error in the analysis of alcohols is ±1%.

The results warrant the conclusion that both *cis*-*trans*-2-methylcycloheptyl acetate are produced mainly through the direct acid-promoted addition of acetic acid to bicyclo[5.1.0]octane. Significantly, the relative amount of *cis*-2-methylcycloheptyl acetate is high (~30%) and at most there is only a slight excess (~10%) of the *trans* isomer. This result deviates from the very high degree of stereoselectivity displayed by bicyclo[3.1.0]hexane, bicyclo[4.1.0]heptane,[9] and derivatives[10,2] on acid-promoted ring opening. The low degree of stereoselectivity which accompanies the opening of bicyclo[5.1.0]octane can be rationalized by a mechanistic scheme which involves the predominance of a carbonium ion process. Carbonium ion mechanisms have been invoked previously to account for results in the opening of the three-membered ring in *exo*-tricyclo[3.2.1.$0^{2,4}$]octane[11] and derivatives of $2\alpha,3\alpha$-methylenecholestane.[12] The slight excess of *trans*-2-methylcycloheptyl acetate may reflect a remnant of the usually prevailing process involving backside nucleophilic solvent attack on a protonated strained carbon–carbon bond. Alternatively, the formation of both *cis*- and *trans*-2-methylcycloheptyl acetate may involve both backside and frontside nucleophilic attack of a protonated bond. For the latter process a number of variations are possible; one of these is the multicenter process which, along with the backside process, is depicted below.[13] The emergence of either the competing frontside attack or the competing carbonium ion process could be attributed to the compression of activation energies resulting primarily from the increased activation energy of a noncollinear backside displacement process. It is not possible to decide between the alternative mechanistic schemes with the data presented herein.

---

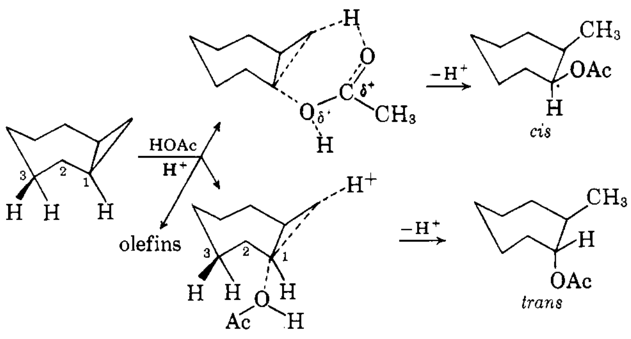
(9) R. T. LaLonde and L. S. Forney, *J. Am. Chem. Soc.*, **85**, 3767 (1963).

(10) R. T. LaLonde and M. A. Tobias, *ibid.*, **85**, 3771 (1963).

(11) R. T. LaLonde and J. J. Batelka, *Tetrahedron Letters*, **9**, 445 (1964).

(12) R. C. Cookson, D. P. G. Hamon, and J. Hudec, *J. Chem. Soc.*, 5782 (1963).

(13) In connection with the proposed frontside nucleophilic attack it is interesting that formolysis of *trans*-bicyclo[6.1.0]nonane affords only *trans*-2-methylcyclooctyl formate as the sole unrearranged ester [A. C. Cope and J. H. Hecht, *J. Am. Chem. Soc.*, **85**, 1780 (1963)]. Should this isomer represent the kinetically controlled product, although it is possible that it does not, the high degree of stereoselectivity in ester formation could be attributed to frontside attack in the manner proposed above. As a Dreiding model of *trans*-bicyclo[6.1.0]nonane illustrates, backside nucleophilic attack would be severely hindered by ring carbon and hydrogen atoms. In addition, inversion of the carbon undergoing nucleophilic attack would be made difficult by the rigidity of the *trans*-bicyclo[6.1.0]nonane ring system.



Two other aspects of the ring-opening results are noteworthy. First, the ring opening is slow compared with the opening of bicyclo[4.1.0]heptane which, under conditions identical with those used for bicyclo[5.1.0]octane, was consumed completely in 24 hr.[9] Bicyclo[5.1.0]octane reacts largely but not completely in 47 hr. A similar disparity in reactivity has been noted in the reactions of cyclohexene and cycloheptene oxides with malonate ion.[14] These differences in reactivity manifest the steric hindrance to backside nucleophilic displacement of epoxide by malonate ion or protonated carbon by solvent in the seven-membered ring systems.

The second noteworthy aspect is the presence of 4-methylcycloheptyl acetate in the mixture of acetates. This product probably arises by way of a transannular hydride shift, the extent of which (12%) is much less than that (97%) reported[15] in the opening of *cis*-bicyclo[6.1.0]nonane. As would be expected, the tendency toward transannular hydride shift in the two bicyclo[*n*.1.0]alkanes parallels the greater tendency for transannular hydride shift in cyclooctene oxide[16,17] compared with cycloheptene oxide.[18] Significantly, the extent to which transannular hydride shift occurs in the opening of bicyclo[5.1.0]octane is greater than the slight amount (2.4%) observed in the opening of cycloheptene oxide under somewhat similar conditions.[18] This observation suggests that the acid-promoted opening of the three-membered ring in bicyclo[5.1.0]octane involves more carbonium ion character than the opening of cycloheptene oxide. On this basis, of the alternative mechanistic schemes mentioned above, the one involving both a carbonium ion and backside nucleophilic solvent participation would be preferred.

Experimental

Reaction of Bicyclo[5.1.0]octane with Acetic Acid.—Bicyclo[5.1.0]octane was prepared from cycloheptene by the method of Simmons and Smith[19]: b.p. 140–141°, n^{25}_{D} 1.4606; lit.[20] b.p. 141.5–142°, n^{25}_{D} 1.4601. A sealed glass tube containing 3.30 g. of bicyclo[5.1.0]octane and 36 ml. of 0.07 *N* sulfuric acid in glacial acetic acid was placed in a constant-temperature bath at 47°. After 47 hr. the contents were subjected to work-up in the usual manner.[9] The material obtained (4.40 g.) was immediately analyzed by gas chromatography using an 8-ft. Carbowax 20 M column at 180°. The chromatogram showed the reaction mixture to consist of 40% olefin and 60% acetate, along with unconverted bicyclooctane (<1%). Qualitative gas chromatographic analysis of the product mixture on a 9-ft. 30% silver nitrate–triethylene glycol on Celite column at 43° established the presence of bicyclo[5.1.0]octane (0.5 min.), 1-methylcycloheptene (2.1 min.), vinylcyclohexane (3.6 min.), and 3-methylcycloheptene (9.7 min.) by a comparison of the chromatographic retention times with retention times of the known olefins. Employing the same chromatographic conditions, the presence of 1-ethylcyclohexene (0.9 min.), ethylidene cyclohexane (1.8 min.), and 4- and 5-methylcycloheptene (7.1 and 8.3 min.) could not be detected. These chromatographic conditions were not suitable for detecting small amounts of cyclooctene (retention time 18.4 min.). Quantitative analysis of the hydrocarbon fraction was performed on a 20% tricresyl phosphate on firebrick column at 11 p.s.i. and 83°. The chromatogram revealed the presence of 1-methylcycloheptene (79%, 12.4 min.), 3-methylcycloheptene (15%, 10.8 min.), vinylcyclohexane (4%, 9.0 min.), and cyclooctene (1%, 17.5 min.). Bicyclo[5.1.0]octane (retention time 15.0 min.) represents <1% of the hydrocarbon fraction. The two major components were trapped and the infrared spectrum of each was identical with the spectra of authentic olefins.

Treatment of 3.80 g. of the crude product mixture with lithium aluminum hydride gave 2.50 g. of an oil whose infrared spectrum showed no carbonyl absorption. The gas chromatogram of the resulting mixture of alcohols was obtained by using a 17% glycerol on Celite column at 102° and showed five peaks. The retention time, estimated per cent amounts, and the alcohols having the identical retention time are 4.5 min., ~40%, 1-methylcycloheptanol, methylcyclohexylcarbinol, and *cis*-2-methylcycloheptanol[21]; 5.4 min., ~40%, *trans*-2-methylcycloheptanol; 6.6 min., <5%, *trans*-3-methylcycloheptanol; 7.6 min., ~15%, *cis*-3-methylcycloheptanol and *cis*- and *trans*-4-methylcycloheptanol; 13.7 min., 4%, cyclooctanol. For all peaks except the one representing cyclooctanol, there was considerable interpeak tailing even under the best chromatographic conditions employing a number of different columns. Consequently, to assess the relative amount of each alcohol it was necessary to estimate the lower portion of the peak boundries. By employing a Castorwax column at 215°, the mixture of alcohols was separated into four components. Peaks were found at 6.1 min. (1-methylcycloheptanol, 4%), 6.7 min. (cyclohexylmethylcarbinol, 8%), 8.0 min. (the isomeric 2-, 3-, and 4-methylcycloheptanols, 86%), and 11.5 min. (cyclooctanol, 2%). Since the sum of 1-methylcycloheptanol, cyclohexylmethylcarbinol, and *cis*-2-methylcycloheptanol was estimated at 38% by chromatography employing glycerol on Celite, the results obtained from chromatography on Carbowax indicated that the amount of *cis*-2-methylcycloheptanol was about 26%.

Bicyclo[5.1.0]octane was treated with sulfuric acid in glacial acetic acid, in precisely the same manner as described above, for periods of 0.5, 1.0, 8, 21, and 44 hr. The chromatographic analyses to determine the ratio of olefin to acetate were carried out as described for the 47-hr. reaction. The analyses for alcohols were carried out using the Castorwax column. Results of these analyses are given in Table I.

Oxidation of the Cycloalkanols.—A portion of the mixture of alcohols (1.52 g.) obtained from the 47-hr. reaction was separated into olefin and alcohol fractions by distillation. The latter fraction (763 mg., b.p. 95–96° at 7 mm.) was dissolved in 10 ml. of acetone and titrated to an orange-brown end point with an 8 *N* solution of chromic anhydride in 30% sulfuric acid. The reaction solution was decanted from the chromium salts and the product was isolated by adding water and extracting with ether. The combined organic layer was washed with 5% sodium bicarbonate solution and brine, and dried over magnesium sulfate. Removal of most of the ether by careful distillation gave 868 mg. of residue possessing infrared bands at 5.85, 6.90, and 7.28 μ. The ketone mixture was analyzed on a Carbowax 20 M column at 168°. The chromatogram showed peaks corresponding in retention times to cyclohexyl methyl ketone (15.2 min., 6%), 2-methylcycloheptanone and 1-methylcycloheptanol (18.4 min., 72%), 3-methylcycloheptanone (20.9 min., 5%), 4-

---

[14] W. Herz and L. A. Glick, *J. Org. Chem.*, **28**, 2970 (1963); **29**, 613 (1964).

[15] A. C. Cope and G. L. Woo, *J. Am. Chem. Soc.*, **85**, 3601 (1963).

[16] A. C. Cope, S. W. Fenton, and C. F. Spencer, *ibid.*, **74**, 5884 (1952).

[17] A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, and G. W. Wood, *ibid.*, **79**, 3900 (1957).

[18] A. C. Cope, T. A. Liss, and G. W. Wood, *ibid.*, **79**, 6287 (1957).

[19] H. E. Simmons and R. D. Smith, *ibid.*, **81**, 4256 (1959).

[20] L. Friedman and H. Schecter, *ibid.*, **83**, 3159 (1961).

[21] Under the same chromatographic conditions, pure 1-methylcycloheptanol and pure methylcyclohexylcarbinol both have a retention time of 4.0 min. but when mixed in small amounts with *cis*-2-methylcycloheptanol, emerge with the last alcohol as a single peak at 4.5 min.

methylcycloheptanone (22.6 min., 12%), and cyclooctanone (28.6 min., 2%). An unidentified peak (4%) appeared at a retention time of 16.9 min. The major ketone was isolated by gas chromatography and its infrared spectrum was identical with the spectrum of 2-methylcycloheptanone with the exception that the spectrum of the trapped ketone showed absorption in the region of 2.9–3.0 μ. 4-Methylcycloheptanone was also separated from the mixture of ketones by gas chromatography and its spectrum was identical to the spectrum of authentic material.

Acknowledgment.—This work was supported in part by a grant from the Research Corporation, New York, New York.

Fused Small-Ring Compounds. I. Synthesis of Some *trans*-Bicyclo[3.2.0]heptanes and *trans*-Bicyclo[4.2.0]octanes[1]

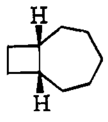
JERROLD MEINWALD, JOSEPH J. TUFARIELLO,[2] AND JEFFREY J. HURST

Department of Chemistry, Cornell University, Ithaca, New York

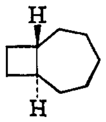
Received March 24, 1964

A nonphotochemical reaction sequence leading to several *trans*-fused bicyclo[3.2.0]heptanes and bicyclo[4.2.0]octanes is described. The chief compounds of interest include *trans*-bicyclo[3.2.0]heptan-3-ol (**21**), *trans*-bicyclo[3.2.0]heptan-3-one (**22**), *trans*-bicyclo[4.2.0]octan-3-one (**27**), and the equatorial and axial forms of *trans*-bicyclo[4.2.0]octan-3-ol (**28** and **31**).

The study of highly strained, *trans*-fused bicyclic compounds has aroused considerable interest in recent years.[3–9] In particular, much attention has been devoted to those structures which incorporate a *trans*-fused cyclobutane moiety. It had been presumed[3] until quite recently that a seven-membered ring is the smallest cycle that can span a cyclobutane ring in a *trans* manner. Indeed, the two possible 7–4 hydrocarbons are known[4] (*i.e.*, *cis*- and *trans*-bicyclo[5.2.0]nonane, **1** and **2**), but it is interesting to note that their physical properties suggest that their heat contents are comparable, if the conformational rule is applicable.[4]

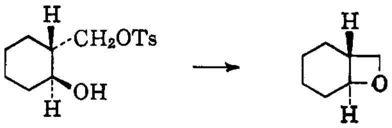


1

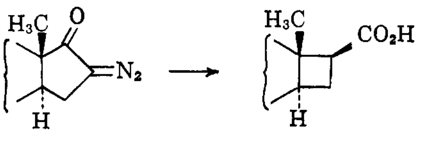


2

In 1961, *trans*-7-oxabicyclo[4.2.0]octane (**3**), an example of a *trans*-fused 6–4 system containing a hetero atom, was prepared[5] in 14% yield by treatment of the hydroxy tosylate **4** with concentrated alkali. Shortly thereafter, four reports[6] appeared outlining the synthesis of several D-norsteroids, substances incorporating a 6–4 *trans* fusion within a steroidal framework. The D-norsteroids (**6**) were made by the irradiation of diazo ketones (**5**), which were readily derived from the appropriate 17-keto steroids.

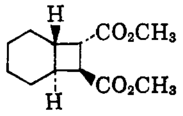


4 **3**

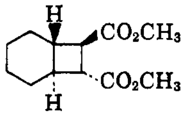


5 **6**

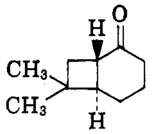
In 1963, the photochemically induced addition of dimethyl maleate to cyclohexene was reported[7] to give a mixture of four diesters, two of which (*i.e.*, **7a** and **7b**) were shown to have a *trans* ring fusion. This remarkable *trans* addition of an olefin to an excited ethylenic system has also been encountered[8] in the preparation of an intermediate utilized in the synthesis of *dl*-caryophyllene. In this case, addition, by photochemical means, of 2-cyclohexenone to isobutylene afforded a mixture of *cis*- and *trans*-7,7-dimethylbicyclo[4.2.0]octan-2-one, with the *trans* isomer **8** comprising *ca.* 80% of the mixture.



7a

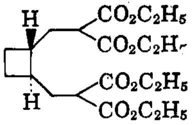


7b



8

There has been only a single report[4] of a *trans*-fused 5–4 system. Alkylation of diethyl malonate with *trans*-1,2-bis(bromomethyl)cyclobutane (**14**, see Chart I), designed to produce the tetra ester **9**, gave as a by-product (*ca.* 16% yield) a substance assigned the *trans* structure **16**.



9

It was our purpose to explore the possibilities of preparing simple derivatives of 5–4 and 6–4 *trans*-fused carbocyclic systems. These systems are of interest in that the *trans* fusion of the five- and six-

---

[1] This work was supported in part by a research grant (no. GM 10090) provided by the National Institutes of Health.

[2] National Institutes of Health Postdoctoral Fellow, 1962–1963.

[3] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 273.

[4] N. L. Allinger, M. Nakazaki, and V. Zalkow, *J. Am. Chem. Soc.*, **81**, 4074 (1959).

[5] O. Kovacs, Z. Tuba, I. Weisz, and G. Schneider, *Chem. Ind.* (London), 1222 (1961).

[6] M. P. Cava and E. Moroz, *J. Am. Chem. Soc.*, **84**, 115 (1962); J. Meinwald, G. G. Curtis, and P. Gassman, *ibid.*, **84**, 116 (1962); J. L. Mateos, O. Chao, and H. Flores R, *Tetrahedron*, **19**, 1051 (1963); G. Muller, C. Huynh, and J. Matheiu, *Bull. soc. chim. France*, 296 (1962).

[7] P. de Mayo, R. W. Yip, and S. T. Reid, *Proc. Chem. Soc.*, 54 (1963).

[8] E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **85**, 362 (1963).

[9] A. C. Cope and J. K. Hecht, *ibid.*, **85**, 1780 (1963).