The Preparation and Ground State Properties of Several Hydro- and Functional Group Derivatives of Bicyclo[2.2.1]heptadiene Containing 7-Spiro Substituents[1]

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The preparation of several hydro- and functional group derivatives of the polycyclic systems bicyclo[2.2.1]heptadiene-7-spiro-1'-cyclopropane (Ib) and bicyclo[2.2.1]heptadiene-7-spiro-1'-cyclopentane (Ic) is reported. A comparison of the infrared spectra of these derivatives and those of the corresponding bicyclo[2.2.1]heptadiene (Ia) derivatives yields a unique band at 9.91 μ which can be identified with the 7-spirocyclopropane ring. Other possible structural correlations for these systems are noted and discussed. The Raman spectra of the olefinic derivatives of Ia, b, and c show anomalous variations in their C=C stretching frequencies. This has led to a reconsideration of the accepted C=C stretching frequency–strain correlation and a new formulation which involves little or no change in force constants but does introduce leading terms of $a + b \cos^2 \beta$ where a and b are constants and β is the C–C–C angle about the double bond. It is shown that this formulation fits the available data and can be made to rationalize the slightly lower C=C stretching frequency observed for derivatives of Ib.

Introduction

As part of a continuing study of the interaction of non-conjugated chromophores,[3] it was of interest to prepare several unsaturated [2.2.1]bicyclic molecules with substituents in the bridge positions. It seemed possible that with properly chosen substituents, the strain in these systems might be significantly altered and thus give further insight into the factors which affect the ultraviolet spectra of non-conjugated chromophores. The substituents selected for incorporation were a 7-spirocyclopropane group and a 7-spirocyclopentane group so that the polycyclic systems to be considered are various hydro and functional derivatives of Ia, Ib and Ic.[4]

Ia   Ib   Ic
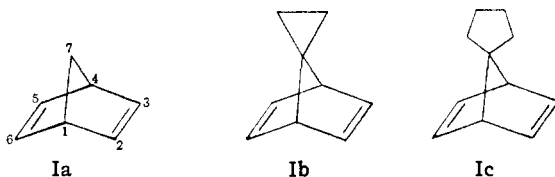
The expected effect of incorporating a 7-spirocyclopropane ring (b-series) was that the 1,4-bridgehead atoms would be spread further apart relative to both the unsubstituted molecules (a-series) and the corresponding 7-spirocyclopentane derivative (c-series). The basis for this expectation is the well-known observation that the external H–C–H angle of cyclopropane compounds is significantly larger than the H–C–H angles in methane or cyclopentane.[5] Since the internal C–C–C bridge angle of bicycloheptadiene[6] is already compressed to 97° and since angle strain increases as

(1) Taken from a dissertation submitted by R. R. Craig to Cornell University for the Ph.D. degree, February, 1960.

(2) Presented at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

(3) (a) C. F. Wilcox, Jr., J. Chem. Phys., 33, 1874 (1960); (b) C. F. Wilcox, Jr., and A. C. Craig. J. Org. Chem., 26, 2491 (1961). Also, (c) C. F. Wilcox, Jr., S. Winstein and W. G. McMillan. J. Am. Chem. Soc., 82, 5450 (1960).

(4) Since in this paper numerous bicyclo[2.2.1]heptanes will be mentioned which differ only by the substituents at the 7-positions it is desirable to adopt the convention that a suffix a to a Roman numeral will always indicate a compound with hydrogens at the bridge positions; a suffix b will indicate a spirocyclopropane substituent; a suffix c will indicate a spirocyclopentane substituent.

(5) G. W. Wheland, "Resonance in Organic Chemistry." John Wiley and Sons, Inc., New York, N. Y., 1955, Appendix.

(6) Unpublished data of V. Schomaker quoted in ref. 1c.

the square of the angle deviation,[7] there are realistic reasons for expecting a significant difference in the strain about the 7-position. This increased strain about the bridge atoms suggests that for this system the bridgehead carbon atoms 1 and 4 will be further apart so that although the total angle strain undoubtedly is larger for the spirocyclopropane compounds, the strain at atoms 2, 3, 5 and 7 is less.

This paper is restricted to a consideration of these differing strain effects on the ground state energies. In a succeeding paper the excited states and the excitation energies will be discussed. This paper will present first the preparation of various derivatives of Ia, b and c followed by a comparison of their infrared spectra. Finally, Raman absorption data on certain of the olefins will be presented with a re-examination of the correlation between double bond stretching frequencies and angle strain. It will be shown that the accepted correlation is in important respects incorrect and is an inadequate measure of strain for the systems at hand and many other highly strained molecules.

Results and Discussion

The various derivatives of Ia, Ib and Ic were prepared by the procedures outlined in Fig. 1 for the specific case of the spirocyclopentane series. These steps are well established for the a-series and require no comment beyond that given in the Experimental section.

The infrared absorption spectra of the twenty-one compounds IIIa, b and c through IXa, b and c were determined as potassium bromide pellets if solid or neat if liquid. Although the spectra were, for the most part, those expected from their structures, there were several interesting features worth noting. The pertinent data are recorded in Table I.

(1) **Dimethyl Maleate Derivatives.**—The six dimethyl maleate derivatives Va, b and c and VIa, b and c showed medium to strong bands at 6.13–6.18 μ in addition to the expected 5.8 μ carbonyl absorption. This band centered on 6.15 μ was either weak or absent in the remaining compounds. As is pointed out later, this band may

(7) F. H. Westheimer, in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 12. The limitations of this dependence are also mentioned in this chapter.

TABLE I

INFRARED ABSORPTION SPECTRA

Compound	6.2-μ region	9.9-μ region	14-μ region	
IIIa	6.18w	....	14.07s	
IIIb	....	9.91m	14.07s	
IIIc	6.15w	....	13.97s	
IVa	....	....	......	
IVb	....	9.89	......	
IVc	....	....	......	
Va	6.13s	....	13.54s	14.01s
Vb	6.16s	9.89m	13.46s	13.85s
Vc	6.14s	....	....	13.79s
VIa	6.17m	....	......	
VIb	6.18m	9.89m	......	
VIc	6.17m	....	......	
VIIa	....	....	13.59	14.34s
VIIb	....	9.92m	13.64	14.34m
VIIc	....	9.88w	....	14.33s
VIIIa	....	9.96w	14.40s	
VIIIb	....	9.94m	14.41s	
VIIIc	....	....	14.41s	
IXa	....	....	14.41ms	
IXb	....	9.90m	14.41ms	
IXc	....	....	14.41ms	

have considerable practical significance since its exact location seems to closely parallel the Raman determined unsubstituted double-bond stretching frequencies.

(2) **Cyclopropane Absorption.**—The existence of a reliable characteristic cyclopropane ring absorption has been questioned.[8] Examination of the spectra of the compounds reported in this study shows, however, that for all of the cyclopropane-containing compounds a medium strength band at 9.91 ± 0.03 μ does occur. The remaining compounds either do not have a band here or else the absorption is weak. From the spectra published by Derfer, et al.,[9] it would appear that his 1,1-dialkyl cyclopropanes also show absorption near 9.9 μ and it is interesting, too, that 7-spirocyclopropane[2.2.1]bicycloheptadiene (Ib) has a medium strength band at 9.95 μ. These consistencies, however, must be viewed cautiously when it is considered that the remaining compounds in this study show strong bands in the closely neighboring region of 9.5–9.8 μ and that 5-spirocyclopentadiene-cyclopropane (IIb) fails to show a band at 9.91 μ but does show strong absorption at 9.77 μ.[10] Although the latter compound is a somewhat special case which could be rationalized, it seems better to draw the more limited conclusion that 7-spirocyclopropane derivatives of [2.2.1]bicyclic systems have absorption at 9.9 μ.

(3) **cis-Olefin Absorption.**—The region of 13.5–14.7 μ has been suggested as characteristic of cis-disubstituted olefins[11] although it has been pointed out the position of the band is variable and other absorptions occur in the same region.[12] These

(8) C. F. H. Allen, T. J. David, W. J. Humphlett and D. W. Stewart, J. Org. Chem., 22, 1291 (1957); A. T. Blomquist and D. T. Longone, J. Am. Chem. Soc., 81, 2012 (1959).

(9) J. M. Derfer, E. E. Pickett and C. E. Boord, ibid., 71, 2482 (1949).

(10) Unpublished work of R. Craig.

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1958, and references therein.
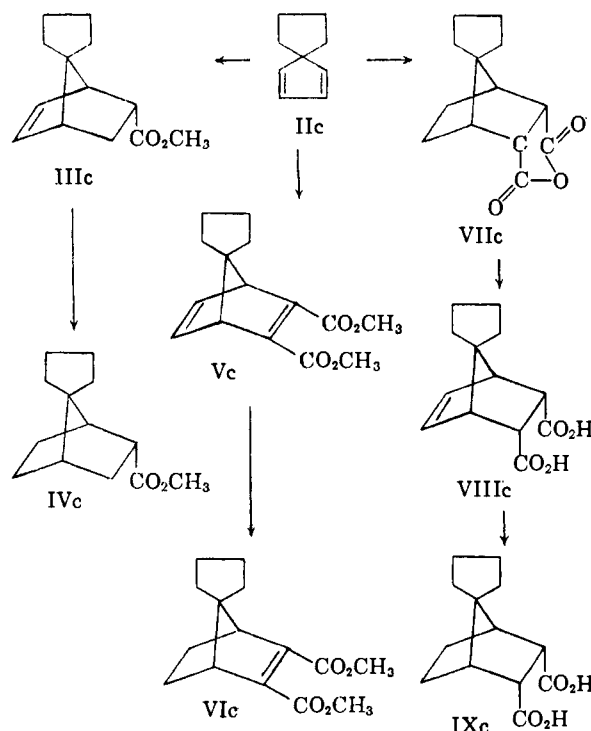
Fig. 1.—Preparative scheme for the spirocyclopentane series.

points are observed in the spectra of the present compounds. Thus, all of the cis-disubstituted olefins show strong absorption in this region. For IIIa, b, c, VIIa, b, c and VIIIa, b and c the bands come at 14.02 ± 0.05, 14.34 ± 0.01 and 14.41 ± 0.01, respectively, whereas for Va, b and c the band is more variable with absorption at 13.90 ± 0.11 μ. The interference of other bands is illustrated by the medium strong bands of IXa, b and c at 14.41 μ. From these results it is not possible to discern any trends which can be associated with varying strain in the double bonds.

According to Kohlrausch[13] a measure of strain in cis-disubstituted olefins is the position of the double bond stretching frequency (usually determined from their Raman spectra because of the weakness of this band in the infrared).

Thus relatively unstrained molecules like cyclohexene absorb near 1650 cm.[-1] while highly strained molecules like bicycloheptane absorb near 1570 cm.[-1]. Kohlrausch further concluded that the rate of change of frequency increased with increasing angle deviation so that the complete "observed" frequency–angle correlation is that shown by the upper curve of Fig. 3.

In Table II are reported the Raman spectra of 50% acetone solutions of IIIa, b, c and Va, b, c for the range 1400–1700 cm.[-1].[14] As pointed out in the Introduction, the cyclopropane series was expected to have higher over-all strain but at the same time less strained double bonds than the

(12) E. R. H. Jones, G. H. Mansfield and M. C. Whiting, J. Chem. Soc., 4073 (1956), and H. B. Henbest, G. D. Meakins, B. Nicholls and R. A. L. Wilson, ibid., 997 (1957).

(13) K. W. F. Kohlrausch, et al., Ber., 69, 729 (1936); 75, 1385 (1942).

(14) It is a pleasure to acknowledge the assistance of Mr. R. Miano in determining these spectra and his release of valuable machine time.
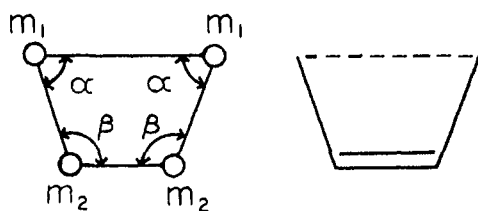
Fig. 2.—Model for *cis* double bond.

unsubstituted reference systems so that from the Kohlrausch correlation one might predict that these cyclopropane compounds would have higher C=C stretching frequencies. The fact is, however, that the cyclopropyl compound Vb shows a small but significant shift to longer wave length relative to the reference systems.[15]

TABLE II

RAMAN FREQUENCIES

Compound	Frequencies, cm.$^{-1}$	Compound	Frequencies, cm.$^{-1}$
Va	1565, 1630	VIa	1624
Vb	1561, 1626	VIb	1621
Vc	1566, 1632	VIc	1627

In order to understand this apparent discrepancy, it is necessary to inquire into the basis of the Kohlrausch frequency–strain correlation. The interpretation favored by Kohlrausch is that as the bonds are bent the force constant decreases (presumably by rehybridization of the sp^2 orbitals) and consequently the frequency also is lowered. Although this effect may well play some role, there is an alternate interpretation which in fact accounts for the older data as well as the present apparent anomaly. This alternative (or additional) interpretation starts with the recognition that an observed stretching frequency is not characteristic of an isolated double bond but, rather, represents a blend of this simple stretch *coupled* with stretches and bends of neighboring bonds. Put another way, the observed frequency is a molecular frequency and not just that of an isolated fragment. From this point of view it is easy to see qualitatively how the coupling constants and consequently the frequency could change with geometry.

As a test of this interpretation a normal coördinate analysis has been carried out for the in-plane symmetrical frequencies of the four particle *cis* double-bond analog in Fig. 2. It is understood that any changes in frequency of the C=C stretch will be determined primarily by the immediate neighborhood of this bond so that this highly simplified model should give a reasonable first approximation to the angular (β) dependence of the stretching frequency. The simultaneous equations in terms of the variables m_1, m_2, α, β and the four different force constants between the masses are given in the Appendix. No direct interaction terms between m_1 and m_2 have been considered. These equations reduce to those of Trinkler,[16]

(15) It is interesting to note that the bands at 1625 cm.$^{-1}$ present in both the infrared and Raman spectra show this same pattern. It would appear that this frequency is associated with the EtCO$_2$—C=C—CO$_2$Et group. This observation is important since it not only tends to confirm the double-bond frequency behavior, but also suggests a new tool for measuring strain in double bonds with infrared spectra instead of with the experimentally less accessible Raman spectra.

(16) Von F. Trinkler, *Proc. Indian Acad. Sci.*, **8A**, 383 (1938).
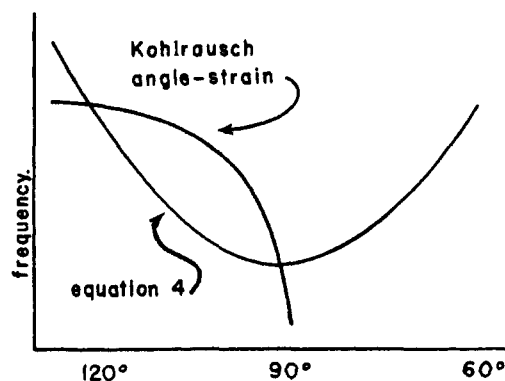

Fig. 3.—A schematic comparison of the different angle dependencies of the C=C stretching frequency.

which he derived for the special case of $\alpha = \beta = 90°$ and also to those of Lechner,[17] which he derived for the special case where the stretching force constant between the m_1's (k_{11}) and the bending constant k_α were zero. With the idea of determining the dependence of the double bond frequency of this model on the various force constants and hence its general applicability to *cis*-disubstituted olefins, an approximate solution for the double bond frequency was developed by perturbation methods (eq. 4 in the Appendix). With $m_1 = m_2 = 13$, $k_{12} = k_{11} = 4.5$, $k_{22} = 9.2$ and $k_\alpha = k_\beta = 0.35$ the double bond frequencies calculated as a function of the angle β by both the exact equations and the approximation method are those given in Table III. It can be seen that for these reasonable values of the force constants the agreement between the exact and approximate solutions is excellent (especially for β near 90° which is the region of interest) so that conclusions drawn from eq. 4 are equally significant. From eq. 4 it is apparent that with reasonable values for the force constants the calculated double bond frequency is not appreciably affected by the force constant between the two m_1's or by the magnitude of m_1, which supports the idea that this simple model should be a good approximation for *cis*-disubstituted olefins.

TABLE III

EFFECT OF ANGLE ON THE CALCULATED STRETCHING FREQUENCIES

Angle β	120°	110°	100°	90°	60°
Exact soln., cm.$^{-1}$	1650	1618	1589	1580	1650
Approx. soln., cm.$^{-1}$	1646	1613	1589	1580	1646

From eq. 4 several significant conclusions can be drawn. First, the C=C stretching frequency decreases as the angle β approaches 90°. This decrease occurs in spite of the fact that no force constants were changed and arises primarily from a decrease in coupling with the single bond m_1–m_2 stretching vibration. Second, the functional form of the dependence of frequency on angle is quite different from that predicted on the basis of only angle strain. This difference is illustrated in Fig. 3. Equation 4 predicts a cos$^2\beta$ dependence of frequency such that at $\beta = 90°$ the coupling and hence the frequency is a minimum.

(17) F. Lechner, *Akad. Wiss. Wien.* (IIa) **141**, 633 (1932).

TABLE IV

DOUBLE BOND STRETCHING FREQUENCIES

Cyclooctene[18]	1673	Bicycloheptene[18]	1568
Cycloheptene[18]	1651	Cyclobutene[18]	1566
Cyclohexene[18]	1646	Cyclopropene[19]	1640
Cyclopentene[18]	1611		

Available data (Table IV) support this predicted angle dependence. Thus although cyclobutene[20] and bicycloheptene[21] have quite different bond angles (ca. 95° and 105°, respectively) they have almost identical stretching frequencies. The stretching frequencies of cyclohexene, cycloheptene, cyclooctene increase in a way that requires only small changes in angles according to eq. 4. Even more dramatic is the stretching frequency of cyclopropene. On the basis of the Kohlrausch idea of angle strain, cyclopropene would be expected to have a very low frequency whereas according to eq. 4 the frequency should approach that of cyclohexene ($\cos^2 120° = \cos^2 60°$). From this excellent agreement of the data with the predictions based on coupling effects alone, it would appear that changes in force constants with angle are not significant for these cis-olefins.[22] The remaining discrepancy of 10 cm.$^{-1}$ in cyclobutene and bicycloheptene could arise from limitations in the model or from small alterations in force constants.

These conclusions offer a simple interpretation of the reversal of the frequency shift in the bridge cyclopropane series. Since the observed double bond frequency of these olefins with β near 90° varies only slightly for small changes in β, it is to be expected that other secondary factors would assume a greater relative importance and could even dominate the simple effect of change in coupling constants discussed above. It is difficult to be specific for such complex molecules, but an example of a possible secondary factor might be an inductively induced decrease in the force constants around the bridgehead atoms by the cyclopropane ring.[25]

(18) R. C. Lord and R. W. Walker, J. Am. Chem. Soc., 76, 2518 (1954).

(19) We wish to thank Professor K. Wiberg for making this value available to us.

(20) E. Goldish, K. Hedberg and V. Schomaker, ibid., 78, 2714 (1956).

(21) The value for bicycloheptene is taken as that of bicyclohepta-diene.[6] A comparison of angles calculated for bicycloheptane (C. F. Wilcox, Jr., ibid., 82, 414 (1960)) with those measured for bicycloheptadiene suggests that introducing double bonds has little effect on bridge angles and hence that using the diene angle for the monoene is an acceptable first approximation.

(22) Although eq. 4 no longer applies, analogous qualitative arguments can be applied to the methyl substituted olefins. Thus the increase in frequency observed with 1-methylcyclopentene (1658 cm.$^{-1}$)[18] and 2-methylcyclohexene (1674 cm.$^{-1}$)[18] can be interpreted as coupling to an additional C–C stretch. With cyclopropene (1640 cm.$^{-1}$)[19] it is found that 1,3,3-trimethylcyclopropene absorbs at 1755 cm.$^{-1}$[23] and that 1,2-dimethylcyclopropene[24] and 1,2,3,3-tetramethylcyclopropene[24] both absorb at 1865 cm.$^{-1}$. Again coupling can be invoked except that here the effect is much greater than with cyclohexene presumably because bond following places the methyl groups more nearly colinear with the double bond.

This same approach can be fruitfully extended to exo-methylene compounds to explain the increase in stretching frequency with smaller rings. Other phenomena such as change in intensity with ring size are equally comprehendable.

(23) G. L. Closs and L. E. Closs, J. Am. Chem. Soc., 83, 1003 (1961).

(24) W. von E. Doering and T. Mole, Tetrahedron, 10, 66 (1960).

Experimental[26]

Dienes. A. Spiro[4.2]hepta-1,3-diene (IIb).—The procedure of Levina, et al.,[27] was modified by the substitution of commercial sodamide with tetrahydrofuran as a solvent in place of the previously used sodium in liquid ammonia. In a typical run 78.1 g. (2.0 moles) of finely divided sodium amide (Farchan Research Laboratories) was added slowly to 500 ml. of tetrahydrofuran and then 66.1 g. (1.0 mole) of freshly distilled 1,3-cyclopentadiene was added dropwise with stirring over a 0.5-hour period. The addition of the diene was adjusted so as to maintain gentle reflux. Some care needs to be exercized at this point since occasionally there was an induction period in this anion formation.

The dropwise addition of 189.0 g. (1.0 mole) of 1,2-dibromoethane was carried out over a 3-hour period and was accompanied by considerable heat evolution. After the reaction mixture had cooled to room temperature overnight the product was isolated in one of two ways.

(1) If a definite layer separation had occurred, the upper organic layer was decanted off and the residual salt was dissolved in ca. 300 ml. of water. The aqueous solution was then extracted three times with 30–60° petroleum ether and the extracts combined with the original organic layer. The combined organic material then was extracted successively with 100-ml. portions of water, 10% hydrochloric acid, and water and finally dried over magnesium sulfate.

(2) If no layer separation was evident, then 750 ml. of water was added and the mixture filtered through fine glass wool to remove the obscuring polymeric material which is formed in the reaction. The isolation then proceeded as above.

After the drying agent was removed by filtration and the solvent by distillation the residual liquid was distilled through a 35 × 1.5 cm. glass helices packed column to yield ca. 50 g. (54%) of IIb, b.p. 113° (737 mm.), n^{25}D 1.5032, $d^{20}{}_4$ 0.8916 (lit. b.p. 57° (100 mm.), n^{20}D 1.5078, $d^{20}{}_4$ 0.8999[27]; 45–47° (93 mm.)[28]; n^{20}D 1.5070.[29]

B. Spiro[4.4]nona-1,3-diene (IIc) was prepared by the procedure of part A with the substitution of 1,4-dibromobutane for the 1,2-dibromoethane. The yield was 29% of IIc, b.p. 45° (15 mm.), n^{25}D 1.4865 (lit. 44–46° (22 mm.), n^{20}D 1.4817[28]; b.p. 52° (10 mm.), n^{20}D 1.4790).[30]

Diels–Alder Adducts with Methyl Acrylate. A. endo-2-Carbomethoxybicyclo[2.2.1]hept-5-ene (IIIa).—The procedure of Roberts, et al.,[31] was followed to obtain a 91% yield of ester, b.p. 40° (1.7 mm.), n^{25}D 1.4725 (lit.[31] b.p. 63.5° (5.2 mm.), n^{25}D 1.4718).

B. endo-2-Carbomethoxybicyclo[2.2.1]hept-5-ene-7-spiro-1'-cyclopropane (IIIb).[32]—Spiro[4.2]hepta-1,3-diene (IIb) (0.38 mole) was combined with methyl acrylate (0.4 mole) in anhydrous ether in the same manner as in part A except that the reaction time was extended to 8 days. After the solvent was removed, the remaining liquid was fractionally distilled through a 75-cm. Podbielniak column to yield 35% of IIIb as a clear, sweet smelling liquid, b.p. 76° (3.9 mm.), n^{25}D 1.4831. Based on consumed diene, the yield was 48%.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.96; H, 7.91.

C, endo-2-Carbomethoxybicyclo[2.2.1]hept-5-ene-7-spiro-1'-cyclopentane (IIIc).[32]—Spiro[4.4]nona-1,3-diene (IIc) (0.21 mole) was combined with methyl acrylate (0.25 mole) in anhydrous ether in the same manner as in part B. After the ether was removed by distillation, the remaining liquid was fractionated through a 75-cm. Podbielniak column

(25) There remains the possibility that the argument for an expected higher frequency in the bridge cyclopropane compounds is incorrect and that they are in fact more strained. The ultraviolet spectra to be discussed in a later paper offer some indirect support for an increase in strain.

(26) Melting points were determined in sealed tubes. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

(27) Levina, Mezentsoba and Lebeda, Zhur. Obschei Khim., 25, 1097 (1955).

(28) B. F. Hallam and P. L. Pauson, J. Chem. Soc., 646 (1958).

(29) K. Alder, et al., Ber., 93, 1888 (1960).

(30) Levina and Tantsireva, Doklady Nauk S.S.S.R., 89, 697 (1953).

(31) J. D. Roberts, et al., J. Am. Chem. Soc., 72, 3122 (1950).

(32) This compound has been assigned the endo configuration by analogy to the corresponding a-series compounds.

to yield 40% of IIIc as a mobile, colorless, sweet-smelling liquid, b.p. 90° (1.7 mm.), $n^{25}D$ 1.4940.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.99; H, 9.10.

Reduction of the Monoesters. A. *endo*-2-Carbomethoxybicyclo[2.2.1]heptane (IVa).—To a solution of 0.42 mole of IIIa in 50 ml. of absolute ethanol was added 0.3 g. of solvent-moistened 10% palladium-on-charcoal. The mixture was shaken on a Parr hydrogenation assembly at *ca.* 24° under 50 lb. pressure of hydrogen. The theoretical amount of hydrogen for one double bond was taken up in about 0.5 hour with no further consumption afterward. After the catalyst was separated by filtration and solvent removed by distillation, the residual liquid was fractionally distilled through a 75-cm. Podbielniak column to yield 88% of IVa as a colorless liquid, b.p. 42° (1.7 mm.), 81° (67 mm.), $n^{26}D$ 1.4625.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.18, 69.96; H, 8.63, 8.90.

B. *endo*-2-Carbomethoxybicyclo[2.2.1]heptane-7-spiro-1'-cyclopropane (IVb).[32]—The olefin IIIb (0.067 mole) was reduced in the same manner as in part A to give an 89% yield of IVb, b.p. 63° (1.6 mm.), $n^{25.5}D$ 1.4731.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.49; H, 8.88.

C. *endo*-2-Carbomethoxybicyclo[2.2.1]heptane-7-spiro-1'-cyclopentane (IVc).[30]—The olefin IIIc (0.039 mole) was reduced in the same manner as in part A to give an 83% yield of IVc, b.p. 96° (1.9 mm.), $n^{25.5}D$ 1.4904.

Anal. Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.54, 75.42, 75.65; H, 10.18, 9.20, 9.20.

Diels-Alder Adducts with Dimethyl Acetylenedicarboxylate. A. 2,3-Dicarbomethoxybicyclo[2.2.1]hepta-2,5-diene (Va).—The Diels-Alder reaction of 23.1 g. (0.351 mole) of IIa with 49.9 g. (0.351 mole) of dimethyl acetylenedicarboxylate was carried out according to the procedure of Diels and Alder[30] to yield 68.2 g. (94%) of Va, b.p. 97.5° (1.6 mm.), $n^{24}D$ 1.4940 (lit.[33] 134°–135° (10–11 mm.)).

B. 2,3-Dicarbomethoxybicyclo[2.2.1]hepta-2,5-diene-7-spiro-1'-cyclopropane (Vb).[32]—The adduction of 32.8 g. (0.356 mole) of IIb with 50.6 g. (0.356 mole) of dimethyl acetylenedicarboxylate was carried out as in part A to yield 73.5 g. (88%) of Vb, b.p. 105° (1 mm.), $n^{25.5}D$ 1.5023.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.75, 66.83; H, 6.06, 6.29.

C. 2,3-Dicarbomethoxybicyclo[2.2.1]hepta-2,5-diene-7-spiro-1'-cyclopropane (Vc).[32]—The adduction of 25.1 g. (0.228 mole) of IIc with 32.4 g. (0.228 mole) of dimethyl acetylenedicarboxylate was carried out as in part A to yield 49.2 g. (82%) of Vc, b.p. 122° (1 mm.), $n^{25}D$ 1.5040.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.70, 68.66; H, 6.93, 6.91.

Reduction of the Dimethyl Acetylenedicarboxylate Adducts. A. 2,3-Dicarbomethoxybicyclo[2.2.1]hepta-2-ene (VIa).—The reduction of 26.3 g. (0.127 mole) of Va with palladium-on-charcoal catalyst was carried out according to the procedure of Diels and Alder to yield 22.7 g. (85%) of VIa, b.p. 96.5° (1.4 mm.), $n^{25}D$ 1.4845 (lit. 132–133° (12 mm.),[33] 135–136° (13 mm.)).[34]

B. 2,3-Dicarbomethoxybicyclo[2.2.1]hept-2-ene-7-spiro-1'-cyclopropane (VIb).—The reduction of 32.1 g. (0.137 mole) of Vb was carried out as in part A to yield 29.0 g. (89%) of VIb, b.p. 109.5–110° (1.5 mm.), $n^{25}D$ 1.4928.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.06; H, 6.83. Found: C, 66.31, 66.45; H, 7.03, 7.23.

C. 2,3-Dicarbomethoxybicyclo[2.2.1]hept-2-ene-7-spiro-1'-cyclopentane (VIc).—The reduction of 24.1 g. (0.092 mole) of Vc was carried out as in part A to yield 21.2 g. (87%) of VIc, b.p. 132° (1.4 mm.), $n^{25}D$ 1.5020.

Anal. Calcd. for $C_{15}H_{20}O_4$: C, 68.19; H, 7.63. Found: C, 68.38, 68.48; H, 7.72, 7.69.

Diels-Alder Adducts with Maleic Anhydride. A. *endo-cis* - 2,3 - Dicarboxybicyclo[2.2.1]hept - 5 - ene Anhydride (VIIa).—The Diels–Alder adduction of 155.2 g. (2.35 moles) of freshly distilled cyclopentadiene (IIa) with 230.4

g. (2.35 moles) of maleic anhydride was carried out in benzene solution according to the directions of Diels and Alder[34] to yield 381 g. (86%) of VIIa, m.p. 161–162° (lit.[34] m.p. 164–165°).

B. *endo-cis*-2,3-Dicarboxybicyclo[2.2.1]hept-5-ene-7-spiro-1'-cyclopropane (VIIb).[32]—The adduction of 25.2 g. (0.27 mole) of IIb with 26.9 g. (0.27 mole) of maleic anhydride in 250 ml. of benzene was carried out according to the procedure of Hallam and Pausen[28] to yield 38.6 g. (74%) of VIIb, m.p. 98.5–99.5° (lit. m.p. 97–98°[28] and 98°[29]).

C. *endo-cis*-2,3-Dicarboxybicyclo[2.2.1]hept-5-ene-7-spiro-1'-cyclopentane (VIIc).[32]—The adduction of 18.0 g. (0.15 mole) of IIc with 14.4 g. (0.15 mole) of maleic anhydride in 200 ml. of benzene was carried out according to the procedure of Hallam and Pausen[28] to yield 31.1 g. (95%) of VIIc, m.p. 101.5–102.5° (lit. m.p. 100–101°,[28] 98°[30]).

Hydrolysis of the Maleic Anhydride Adducts. A. *endo-cis*-Dicarboxybicyclo[2.2.1]hept-5-ene (VIIIa).—The hydrolysis of 100 g. (0.61 mole) of VIIa in water was carried out according to the procedure of Diels and Alder[34] to yield 104.1 g. (93%) of VIIIa, m.p. 173–175° (lit[34] m.p. 177–179°).

B. *endo-cis*-Dicarboxybicyclo[2.2.1]hept-5-ene-7-spiro-1'-cyclopropane (VIIIb).[32]—The hydrolysis of 27.3 g. (0.14 mole) of VIIb was accomplished by refluxing with 27 g. of sodium hydroxide in 300 ml. of water for 1 hour. Acidification of the solution with dilute hydrochloric acid yielded 29.9 g. (75%) of VIIIb, m.p. 166–167°.

Anal. Calcd. for $C_{11}H_{12}O_4$: C, 63.46; H, 5.77. Found: C, 62.95; H, 5.62.

C. *endo-cis*-Dicarboxybicyclo[2.2.1]hept-5-ene-7-spiro-1'-cyclopentane (VIIIc).[32]—The hydrolysis of 23.9 g. (0.10 mole) of VIIc was carried out as in part B to yield 22.4 g. (80%) of VIIIc, m.p. 175–176.5° dec. (lit.[28] m.p. 180° dec.).

Reduction of the Diacids. A. *endo-cis*-2,3-Dicarboxybicyclo[2.2.1]heptane (IXa).—The reduction of 40 g. (0.22 mole) of VIIIa in a sodium carbonate solution with a palladium catalyst was carried out according to the procedure of Diels and Alder[34] to yield 25.2 g. (36%) (no attempt was made to concentrate the mother liquors), m.p. 159–160° dec. (lit.[14] m.p. 160–161°).

B. *endo-cis*-2,3-Dicarboxybicyclo[2.2.1]heptane-7-spiro-1'-cyclopropane (IXb).[32]—The reduction of 10.0 g. (0.048 mole) of VIIb was carried out as in part A to yield 10.08 g. (80%) of IXb, m.p. 176–177° dec.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 63.08; H, 7.01.

C. *endo-cis*-2,3-Dicarboxybicyclo[2.2.1]heptane-7-spiro-1'-cyclopentane (IXc).[32]—The reduction of 10.0 g. (0.042 mole) of VIIIc was carried out as in part A to yield 8.3 g. (83%) of IXc, m.p. 168–169° dec.

Anal. Calcd. for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 66.55; H, 8.10.

Appendix

$$\lambda_1 + \lambda_2 + \lambda_3 = 2\frac{k_{11}}{m_1} + 2\frac{k_{22}}{m_2} + 2\frac{k_{12}}{\mu} + \frac{d_1}{\mu} + \frac{d_2}{\mu} \quad (1)$$

$$\lambda_1\lambda_2 + \lambda_1\lambda_3 + \lambda_2\lambda_3 = \frac{k_{12}(d_1 + d_2)}{\mu^2} + 2\frac{k_{11}k_{12}}{m_1m_2}\left(1 + \right.$$

$$\frac{m_2}{m_1}\sin^2\beta\right) + 4\frac{k_{11}k_{22}}{m_1m_2} + 2\frac{k_{11}(d_1 + d_2)}{m_1m_2}\left(1 + \frac{m_2}{m_1}\cos^2\beta\right) +$$

$$2\frac{k_{22}k_{12}}{m_1m_2}\left(1 + \frac{m_1}{m_2}\sin^2\beta\right) + 2\frac{k_{22}(k_1 + k_2)}{m_1m_2}\left(1 + \frac{m_1}{m_2}\cos^2\beta\right)$$
$$(2)$$

$$\lambda_1\lambda_2\lambda_3 = 2\frac{(k_{11} + k_{22})(d_1 + d_2)}{m_1}k_{12} +$$

$$\frac{4k_{11}k_{12}}{m_1m_2\mu}(k_{12}\sin^2\beta + (d_1 + d_2)\cos^2\beta) \quad (3)$$

where

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

k_{ij} is the force constant between masses i and j, d_1 is the bending constant around m_1, d_2 is the bending constant around m_2, and $\lambda_i = 4\pi^2\nu_i^2$.

(33) O. Diels and K. Alder, *Ann.*, **490**, 236 (1931).

(34) O. Diels and K. Alder, *ibid.*, **460**, 98 (1927).

An approximate solution to 1, 2 and 3 based on perturbation methods is

$$\lambda \; (C{=}C) \; = f_3 + \frac{[(k_{12} - d_1 - d_2)\cos^2\beta + (d_1 + d_2)]^2}{m_1 m_2 \, (f_3 - f_2)} +$$

$$\frac{(k_{12} - d_1 - d_2)^2}{m_1 m_2 (f_3 - f_1)} \left(1 + \frac{m_2}{m_1}\right) \sin^2\beta \cos^2\beta \quad (4)$$

where

$$f_3 = \frac{(k_{12} - d_1 - d_2)\cos^2\beta + 2k_{22} + d_1 + d_2}{m_2}$$

$$f_2 = \frac{(k_{12} - d_1 - d_2)\cos^2\beta + 2k_{11} + d_1 + d_2}{m_1}$$

$$f_1 = \frac{[(k_{12} - d_1 - d_2)\sin^2\beta + d_1 + d_2][1 + m_2/m_1]}{m_2}$$

[Contribution from the Research and Development Department, American Oil Co., Whiting, Ind.]

Transsulfonation in Preparing Aromatic Sulfones

By Harald Drews, Seymour Meyerson and Ellis K. Fields

The reaction of an arenesulfonic acid with an arene has generally been assumed to give the sulfone derived from both reactants. However, treating p-toluenesulfonic acid with o-xylene gives considerable dixylyl sulfone in addition to tolyl xylyl sulfone. Likewise, p-xylenesulfonic acid with toluene gives ditolyl and dixylyl sulfones in a total yield almost as great as that of the expected tolyl xylyl species. Further, the product mixture contains also p-xylene and p-toluenesulfonic acid. Because the over-all reaction involves the transfer of a sulfonic acid group from one hydrocarbon to another, it is referred to as "transsulfonation." It is a new addition to the class of reactions—such as transcarbonylation and transbenzylation—in which functional groups are transferred from one aromatic nucleus to another.

A general method for preparing diaryl sulfones was described by Meyer[1] nearly forty years ago. He claimed that symmetrical diaryl sulfones result from reaction of sulfuric acid with an arene, and that unsymmetrical sulfones result from reaction of an arenesulfonic acid with another arene. For example, he reported that m-xylenesulfonic acid with toluene gives p-tolyl m-xylyl sulfone
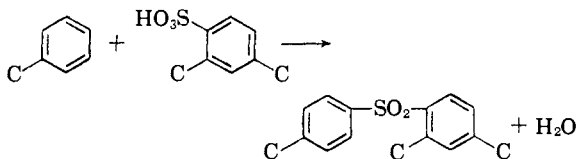
However, the reaction of p-xylenesulfonic acid with toluene actually gives ditolyl and dixylyl sulfones, besides the expected p-tolyl xylyl sulfone and its o-tolyl isomer.[2]

This unexpected result appears to involve "transsulfonation," that is, the transfer of a sulfonic acid group from one aromatic nucleus to another. The scope of transsulfonation has therefore been explored by treating three arenesulfonic acids separately with four different arenes, treating an arenesulfonic acid with a sulfone, and pyrolyzing two arenesulfonic acids. In three further experiments, one essential feature of the Meyer procedure was altered—in two cases, by using a lower temperature; in the third, by not removing the water formed in the reaction—and the reaction mixture was examined for evidence of transsulfonation. Identification of reaction products was made possible by new analytical tools not available to Meyer.

Experimental

The transsulfonation studies were carried out in a reaction flask in which hydrocarbon vapor was passed through a molten sulfonic acid.[1] Excess hydrocarbon together with entrained water from the reaction was continuously condensed, dried over calcium chloride, vaporized, and recycled to the sulfonic acid.

All reasonable efforts were made to ensure high purity of starting materials. Toluene and benzene, Mallinckrodt analytical reagent grade, and Phillips Pure grade o-xylene were found by gas chromatography to be free of the other homologs and were used without further treatment. Eastman p-toluenesulfonic acid was recrystallized from dilute hydrochloric acid to remove benzenesulfonic acid. Eastman benzenesulfonic acid contained traces of p-toluenesulfonic acid not removable by fractional recrystallization. p-Xylenesulfonic acid was prepared by sulfonation of p-xylene, Matheson Coleman & Bell, found by gas chromatography to be free of toluene and benzene. The acid was recrystallized twice from dilute hydrochloric acid; it contained two moles of water, melted at 83°, and had an acid number of 250. Toluenesulfonyl chloride and the xylenesulfonyl chlorides, Eastman white label grade, were used as purchased for synthesis of authentic sulfones.

Products were analyzed by appropriate physical methods: hydrocarbons by gas chromatography; sulfonic acids by infrared absorption; and sulfones by mass spectrometry. The last method was found to be highly sensitive, not only to differences in molecular weight, but also to structural differences among isomeric sulfones.

To calibrate the mass spectrometer, seven authentic sulfones were synthesized by the Friedel-Crafts reaction of a sulfonyl chloride with an aromatic hydrocarbon,[3,4] as summarized in Table I. In a typical synthesis, 100 g. of 2,5-dimethylbenzenesulfonyl chloride dissolved in 120 ml. of p-xylene was dropped into a 1-liter four-necked flask containing 200 ml. of p-xylene and 30 g. aluminum chloride, maintained as a slurry by rapid stirring, at 35° over 1 hour. During addition of the sulfonyl chloride, 50 g. more of aluminum chloride was added in two portions. The reaction mixture was then heated for 2 hours at 65° and poured onto crushed ice. The sulfone was collected on a filter; crystallization from alcohol gave 78.6 g. of product melting at 138°. After two more crystallizations from alcohol, it melted at 144°. The mass spectrum revealed no components other than dixylyl sulfone.

Six sulfones not reported in Table I were also used in calibration. Diphenyl and di-p-tolyl sulfones were Eastman products, recrystallized. Synthesis of the others—di-o-tolyl, o-tolyl p-tolyl, p-xylyl o-tolyl and m-xylyl p-tolyl sulfones—will be reported in a subsequent publication.

Meyer's procedure[1] was employed in preparing sulfones by the reaction of an arenesulfonic acid with an arene. In a typical experiment, 225 g. of p-xylenesulfonic acid dihydrate was heated for 6 hours at 100° at about 130 mm. to dehydrate the acid. The anhydrous acid was put in the recycle apparatus and toluene was circulated through the

(1) H. Meyer, Ann., 433, 327 (1923).

(2) H. Drews, S. Meyerson and E. K. Fields, Angew. Chem., 72, 493 (1960).

(3) S. C. J. Olivier, Rec. trav. chim., 33, 91 (1914); 35, 109 (1915).

(4) G. Holt and B. Pagdin, J. Chem. Soc., 2508 (1960).