Unsaturated Neopentyl Compounds. The Effect of Methyl Substitution on the Solvolytic Course of Homoallenic Brosylates

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Abstract: The acetolysis products of a series of 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonates with methyl substituents at C-3 and/or C-5 have been determined at 40 or 55°. In the absence of a methyl substituent at C-3, the starting brosylates yield rearranged allenic products exclusively: 2-methyl-4,5-hexadien-2-yl acetate, 2-methyl-2,4,5-hexatriene, and/or 2-methyl-1,4,5-hexatriene with one or two methyl substituents at C-5. When the starting brosylate has a methyl substituent at C-3, the acetolysis also yields cyclobutane-ring-containing acetates and hydrocarbons, as well as conjugated and/or cross-conjugated rearranged acyclic nonallenic trienes. The effect of methyl substituents on the acetolysis course of these homoallenic neopentyl-type brosylates is compared with similar effects reported previously for the solvolysis of other homoallenic arenesulfonates which exhibit π-electron participation and it is concluded that the initial intermediate is a cyclopropylcarbinyl-type vinyl cation in each case. It is suggested that the nonallenic acyclic trienes which are observed when the starting neopentyl-type homoallenic brosylate also contains a methyl group at C-3 result from an unusual 1,4-hydride shift in the initial *gem*-dimethyl-cyclopropylcarbinyl-type vinyl cation which is followed by a 1,5-proton shift and/or proton loss and in some cases by a 1,5- or 1,7-sigmatropic hydrogen shift.

It has been apparent for some time that the nature of the products which are formed during the solvolysis of a homoallenic compound is highly dependent upon the structure of the starting material. The solvolyses of appropriate derivatives of the parent alcohol, 3,4-pentadienol (1-OH), are reported to yield mixtures of unrearranged and cyclopropane-ring-containing compounds.[1] Similar mixtures have been described when the parent arenesulfonate carries a methyl substituent at C-1 (2-OTs)[2a] or at C-5 (5-ONps).[1] However when the starting material has a methyl substituent at C-3 (4-OTs) no cyclopropyl products are reported, instead unrearranged and cyclobutyl-type compounds are formed.[2b] If the starting material has an alkyl substituent at C-1 and C-3 (7- and 8-OTs)[2b] or at C-2 and C-3 (10-OTs)[2b] complex mixtures of cyclic and acyclic derivatives are formed. In contrast to these nonneopentyl systems the solvolyses of homoallenic arenesulfonates having two methyl substituents at C-2, *viz.*, 3-OBs,[3] 9-OTs,[4a] and 11-, 13-, or 14-OTs,[5] produce no cyclic products but only unrearranged and/or rearranged acyclic derivatives.

Complementary to our investigation of the effect of methyl substitution on the reactivity of homoallenic neopentyl-type brosylates reported in the preceding paper,[6] we have examined the effects of such methyl substitutions on the nature of the products formed in the acetolysis of 6-, 9-, 12-, 15-, and 18-OBs.[7] We wish to report our results and to offer a rationale for the various alkyl substitution effects which have been observed in the solvolysis of homoallenyl derivatives.

(1) (a) M. Hanack and J. Häffner, *Tetrahedron Lett.*, 2191 (1964); (b) *Chem. Ber.*, **99**, 1077 (1966).

(2) (a) M. Bertrand and M. Santelli, *Compt. Rend.*, **259**, 2251 (1964); (b) *ibid.*, **266**, 231 (1968).

(3) R. S. Bly, A. R. Ballentine, and S. U. Koock, *J. Amer. Chem. Soc.*, **89**, 6993 (1967).

(4) (a) T. L. Jacobs and R. Macomber, *Tetrahedron Lett.*, 4877 (1967); (b) R. S. Macomber, Ph.D. Thesis, Department of Chemistry, University of California, Los Angeles, 1968.

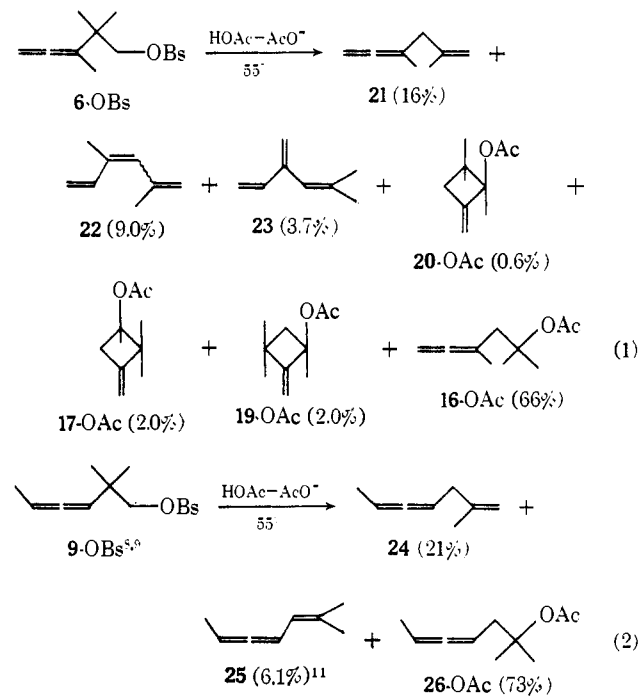(5) R. Garry and R. Vessière, *Bull. Soc. Chim. Fr.*, 1542 (1968).

(6) R. S. Bly and S. U. Koock, *J. Amer. Chem. Soc.*, **90**, 3292 (1969).

(7) To minimize confusion those homoallenic neopentyl brosylates whose reactivity was discussed in the preceding paper[6] have been given the same numbers here.
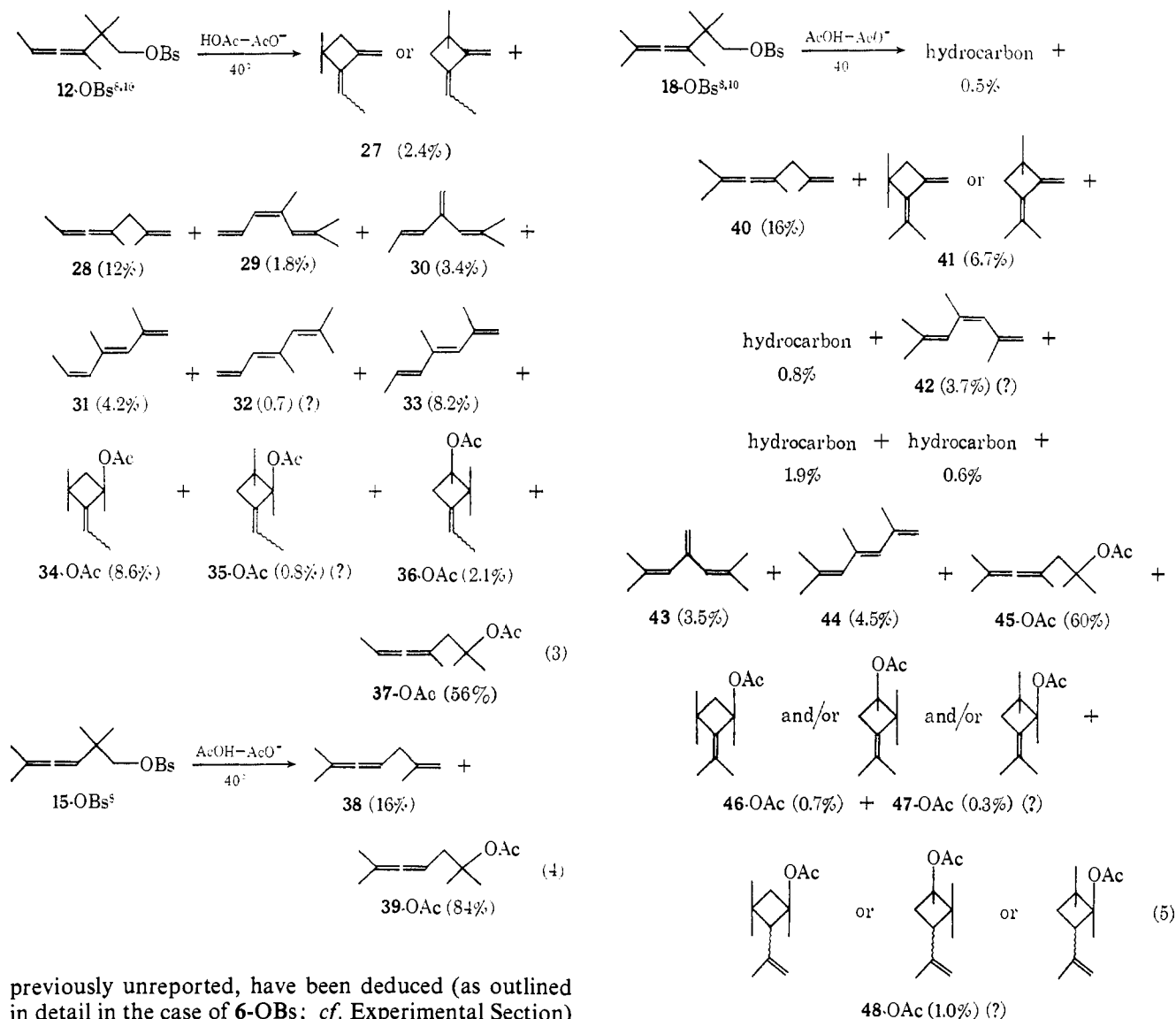
Methods and Results

The starting materials were synthesized as described previously.[6] Insofar as possible the product studies were carried out under conditions identical with those employed in the kinetic determinations. The product compositions were determined by gas–liquid partition chromatography (glpc) in the manner described previously.[3] Although the relative proportions of the acetates are invariant from one to >10 half-lives, the composition of the olefins produced appears in some cases to depend slightly upon the time of reaction.

The structures of the acetolysis products from 6-, 9-,[8,9] 12-,[8,10] 15-,[8] and 18-OBs,[8,10] many of which are

$$6\text{-OBs} \xrightarrow[55°]{HOAc-AcO^-} 21\,(16\%) + 22\,(9.0\%) + 23\,(3.7\%) + 20\text{-OAc}\,(0.6\%) + 17\text{-OAc}\,(2.0\%) + 19\text{-OAc}\,(2.0\%) + 16\text{-OAc}\,(66\%) \quad (1)$$

$$9\text{-OBs}^{5,6} \xrightarrow[55°]{HOAc-AcO^-} 24\,(21\%) + 25\,(6.1\%)^{11} + 26\text{-OAc}\,(73\%) \quad (2)$$

(8) Details are given in the Ph.D. Thesis of S. U. Koock, Department of Chemistry, University of South Carolina, 1968.

(9) Jacobs and Macomber[4] who have investigated the solvolysis of

12-OBs[5,10] $\xrightarrow[40^\circ]{\text{HOAc}-\text{AcO}^-}$ 27 (2.4%)

28 (12%) + 29 (1.8%) + 30 (3.4%) +

31 (4.2%) + 32 (0.7) (?) + 33 (8.2%) +

34-OAc (8.6%)   35-OAc (0.8%) (?)   36-OAc (2.1%) +

OAc

37-OAc (56%)   (3)

15-OBs[5] $\xrightarrow[40^\circ]{\text{AcOH}-\text{AcO}^-}$ 38 (16%) +

39-OAc (84%)   (4)

18-OBs[3,10] $\xrightarrow[40]{\text{AcOH}-\text{AcO}^-}$ hydrocarbon +   0.5%

40 (16%) + 41 (6.7%)   or

hydrocarbon +   42 (3.7%) (?) +
0.8%

hydrocarbon + hydrocarbon +
1.9%   0.6%

43 (3.5%) + 44 (4.5%) + 45-OAc (60%) +

46-OAc (0.7%) + 47-OAc (0.3%) (?)   and/or ... and/or

48-OAc (1.0%) (?)   (5)

previously unreported, have been deduced (as outlined

previously unreported, have been deduced (as outlined in detail in the case of 6-OBs; cf. Experimental Section) from spectral and, where feasible, combustion data determined on the pure collected components and are summarized in eq 1–5, respectively.[12]

We do not intend to imply that all of the structures suggested for the products in eq 1–5 are unequivocally correct, only that they appear to be the most likely ones on the basis of the spectral evidence, usually ir, uv, and nmr, presently available. It is probable that some of the hydrocarbons are not actually produced initially in the acetolysis but instead are formed by a further rearrangement during the latter stages of the reaction or during the isolation. Because of the extreme ease with which the conjugated hexatrienes polymerize some are doubtless lost in this manner during the isolation so that the glpc analyses may not reflect their true abundance in the product mixture.

9-OBs for 10 half-lives at 65° in buffered acetic acid report the formation of 55% 26-OAc, 16% 24, 18% 25, and 11% of at least two other conjugated dimethylhexatrienes.

(10) The question marks after the yields indicate structures inferred on the basis of incomplete spectral data; cf. Experimental Section.

(11) May be contaminated with some 2-methyl-cis,cis-1,3,5-heptatriene; cf. Experimental Section.

(12) In order of appearance from a Carbowax 20M column. Per cents represent relative peak areas normalized to 100 and are uncorrected for differences in thermal conductivity; cf. A. E. Messner, D. M. Rosie, and P. A. Argabright, Anal. Chem., 31, 230 (1959).

Discussion

The Nature of the Initial Intermediate. The effects of the various methyl substitutions on the types of products formed in the solvolyses of homoallenic neopentyl-type brosylates, together with the data cited earlier for the nonneopentyl homoallenic derivatives (cf. Introduction), are summarized in Table I.

It is apparent from our data and from those of Jacobs and Macomber[4] and of Garry and Vessière[5] that homoallenic derivatives having two methyl substituents at C-2, i.e., those of the neopentyl type, do not yield cyclopropyl derivatives upon solvolysis. If they have no alkyl substituent at C-1 or C-3, these neopentyl types produce rearranged acyclic compounds exclusively, cf. 3-, 9-, and 15-OArs. If they carry an alkyl substituent at C-1, i.e., 11-, 13-, and 14-OTs, they give both rearranged and unrearranged acyclic derivatives. Only if a substituent is also present at C-3 do cyclobutyl compounds appear to be formed in appreciable amounts, cf. 6-, 12-, and 18-OBs. Significantly, none of the neopentyl derivatives appear to yield any methyl-migrated products.

Product data alone can only reflect the net time-averaged symmetry of the intermediate(s) not the manner in which such symmetry is achieved and con-

Table I. Types of Products Found in the Solvolysis of Simple Homoallenic Derivatives

R_5'	R_5	R_3	R_2'	R_2	R_1	Compd	Conditions	Cyclopropyl	Acyclic — Unrearranged	Acyclic — Rearranged	Cyclobutyl	Ref
H	H	H	H	H	H	1-Br	H_2O + Ag_2O; 20°	39		53		1[b]
						1-ONps[c]	1:1 acetone-H_2O;[d] 60°	37		52		1[e]
							CH_3OH;[d] 60°			92		1[f]
							AcOH-AcO⁻; 60°	20		61		1[g,h]
							HCOOH-HCOO⁻; 60°	80		5		1[i]
H	H	H	H	H	CH_3	2-OTs	H_2O-AcOH-AcO⁻; 80°	67	30			2a[h,i]
H	CH_3	H	H	H	H	5-ONps[c,h]	1:1 acetone-H_2O; 60°	40		23		1[k]
							HCOOH-HCOO⁻; 70°	51		13		1[l]
H	H	CH_3	H	CH_3	H	10-OTs	H_2O-AcOH-AcO⁻; 80°?	5	Trace	4	91	2b
H	H	CH_3	H	H	CH_3	7-OTs	H_2O-AcOH-AcO⁻; 80°	3		4	73	2b[m]
H	H	CH_3	H	H	$CH(CH_3)_2$	8-OTs	H_2O-AcOH-AcO⁻; 80°?		20	45	17	2b[n]
H	H	CH_3	H	H	H	4-OTs	H_2O-AcOH-AcO⁻; 80°?			30	70	2b[h]
H	H	H	CH_3	CH_3	CH_3	11-OTs	H_2O-AcOH-AcO⁻; 80°		10	90		5
H	H	H	CH_3	CH_3	C_2H_5	13-OTs	H_2O-AcOH-AcO⁻; 80°		42	58		5
C_2H_5	CH_3	H	CH_3	CH_3	CH_3	14-OTs	H_2O-AcOH-AcO⁻; 80°		26	74		5
H	H	H	CH_3	CH_3	H	3-OBs	1:1 acetone-H_2O; 55°			>85		3[o]
							EtOH;[p] 55°			95		3[q]
							AcOH-AcO⁻; 55°			100		3
H	CH_3	H	CH_3	CH_3	H	9-OBs	AcOH-AcO⁻; 55°			100		r
							AcOH-AcO⁻; 65°			89		4[s]
						9-OTs	AcOH-AcO⁻; 65°			90		4[t]
CH_3	CH_3	H	CH_3	CH_3	H	15-OBs	AcOH-AcO⁻; 40°			100		r
H	H	CH_3	CH_3	CH_3	H	6-OBs	AcOH-AcO⁻; 55°			96	4	r
H	CH_3	CH_3	CH_3	CH_3	H	12-OBs	AcOH-AcO⁻; 40°			86	14	r
CH_3	CH_3	CH_3	CH_3	CH_3	H	18-OBs	AcOH-AcO⁻; 40°			87	9	r[u]

[a] Rounded off to the nearest per cent and normalized to 100. [b] Plus 8% of unidentified, unsaturated hydrocarbon(s). [c] ONps = β-naphthalenesulfonate. [d] Buffered with calcium carbonate. [e] Plus 11% of unidentified, unsaturated hydrocarbon(s). [f] Plus 8% of three unidentified compounds. [g] Plus 7 and 12%, respectively, of two unidentified compounds. [h] But see ref 4b. [i] Plus 15% of two unidentified compounds. [j] Plus 3% of unidentified hydrocarbon(s). [k] Plus 32 and 5%, respectively, of unidentified, unsaturated hydrocarbon(s) and other materials. [l] Plus 36% of unidentified unsaturated hydrocarbon. [m] Plus 20% of products unaccounted for. [n] Plus 18% of unidentified materials. [o] Plus <15% of unidentified hydrocarbons. [p] Buffered with pyridine. [q] Plus 5% of an unidentified hydrocarbon. [r] This work. [s] Plus 11% of two unidentified conjugated (?) trienes. [t] Plus 10% of two unidentified, conjugated (?) trienes. [u] Plus 4% of four unidentified hydrocarbons.

sequently do not usually suffice to establish the character of the initial intermediate in a solvolytic reaction. Thus the nature of the products shown in Table I can be understood about as well whether the initial intermediate is a rapidly equilibrating pair of bicylobutonium ions,[4] a rapidly equilibrating pair of homoallenyl cations,[4a] or a cyclopropylcarbinyl-type vinyl cation.[3,4a,6,13,14] Since our rate data[6] in the neopentyl cases imply that much if not all of the developing charge in the transition state is either localized at C-4 or distributed between C-1 and C-4, we prefer the latter formulation. In accord with recent theoretical,[15,16] spectroscopic,[17] and solvolytic[18,19] investigations of the

related cyclopropylcarbinyl cation, we picture this cyclopropylcarbinyl-type vinyl cation (49) in its "bisected" conformation.[20]

Although the kinetic and product data are not always as clear cut in the nonneopentyl cases,[1–3] i.e., where R_2 and/or R_2' are hydrogen, it is likely that an intermediate such as 49 is formed initially in the reactions of all homoallenic derivatives which solvolyze with π-electron participation (Scheme I). When the cyclopropyl ring in 49 carries no alkyl substituent, e.g., in the case of 1- and 5-Z, the initial cation (R_1, R_2, R_2', R_3 = H) is relatively stable and reacts to yield cyclopropane-ring-containing products (path B) exclusively (Table I) or predominantly.[4b,21] When 49 has a single alkyl substituent at C-1, e.g., 2-OTs (R_1 = CH_3), path B is still the major reaction course though some ring opening to a secondary acyclic cation (51) and ring enlargement to a cyclobutyl cation (path C)[4b] may occur. In the neopentyl cases when R_2 and R_2' are methyl and R_3 is hydrogen (e.g., 3-, 9-, 11-, 13-, 14-, and 15-Z) the gem-dimethyl-substituted cyclopropyl ring of 49 is unstable with respect to the ring-opened

(13) The recent studies of Jacobs and Macomber[4] and of Bertrand and Santelli[14] which demonstrate that the acetolysis or "gentle hydrolysis" of optically active homoallenic arenesulfonates (−)-9-OBs and (−)-2-OBs, respectively, yield some active products imply that the intermediates do not attain C_s symmetry, a condition that could be fulfilled equally well by any of the alternate formulations mentioned.

(14) M. Bertrand and M. Santelli, Chem. Commun., 718 (1968).

(15) (a) R. E. Davis and A. Ohno, Tetrahedron, 24, 2063 (1968); (b) K. B. Wiberg, ibid., 24, 1083 (1968); (c) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, as cited in the text and in footnote 20 of ref 15a.

(16) J. E. Baldwin and W. D. Fogelsong, J. Amer. Chem. Soc., 90, 4311 (1968).

(17) G. A. Olah, M. B. Comisaro, C. A. Cupas, and C. U. Pittman, ibid., 87, 2997 (1965); C. U. Pittman, Jr., and G. A. Olah. ibid., 87, 2998, 5123 (1965); N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, ibid., 87, 3000 (1965); N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, ibid., 87, 4533 (1965); G. L. Closs and H. B. Klinger, ibid., 87, 3265 (1965); H. C. Brown and J. D. Cleveland, ibid., 88, 2051 (1966).

(18) P. von R. Schleyer and G. W. Van Dine, ibid., 88, 2321 (1966).

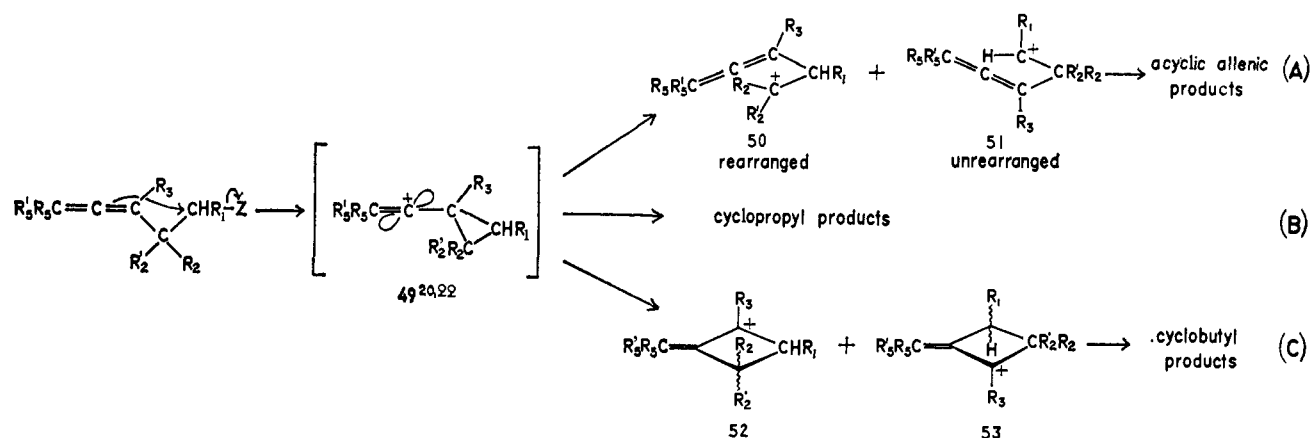(19) K. B. Wiberg and A. J. Ashe, III, Tetrahedron Lett., 1553, 4245 (1965); J. Amer. Chem. Soc., 90, 63 (1968).

(20) For convenience and simplicity we will represent these cyclopropylcarbinyl-type vinyl cations, 49, in the "classical" manner, but do not intend to imply that they are not stabilized by electron donation from the ring.

(21) As the medium is made less nucleophilic and more solvolyzing the proportion of cyclopropyl derivative(s) is increased in each case (Table I), hence it appears that in these nonneopentyl systems where R_1 is H the acyclic materials which are present result from a competing bimolecular displacement by the solvent.

Scheme I

$R_5'R_5C=C=C \overset{R_3}{\underset{R_2' \; R_2}{\diagdown}} CHR_1 \overset{\alpha}{\underset{Z}{\longrightarrow}} \left[R_5'R_5C \overset{+}{=}C \overset{R_3}{\underset{R_2'R_2C}{\diagdown}} CHR_1 \right]$

49 [20,22]

(A) acyclic allenic products — **50** rearranged, **51** unrearranged

(B) cyclopropyl products

(C) ·cyclobutyl products — **52**, **53**

tertiary or (when R_1 is also alkyl) secondary cations, **50** and **51**, respectively, and ring opening (path A) is the exclusive reaction.[23] In those cases where R_3 is methyl (e.g., **4-, 6-, 7-, 8-, 10-, 12-,** and **18-Z**), ring enlargement (path C) to the tertiary cyclobutyl-type cations **52** and **53** becomes important. The small

The Source of the Acyclic Trienes. The acyclic hydrocarbons produced in the acetolysis of the neopentyl-type homoallenic brosylates may be thought of as hexatrienes which carry one or more methyl substituents depending upon the extent of methyl substitution in the starting material and can be divided into five categories:

Table II. Types of Hexatrienes Found in the Acetolysis of Homoallenic Neopentyl Brosylates[a]

$R_5'\diagdown C=C=C \overset{H_3C \diagup C \diagdown CH_3}{\underset{R_3}{\diagup}} CH_2{-}OBs \longrightarrow$ Products

R_5'	R_5	R_3	Compd	56	57	58	59	60
H	H	H	3-OBs[c]	>12[d]	<11[d,e]			
H	CH₃	H	9-OBs[f]	21	6.1[g]			
CH₃	CH₃	H	15-OBs	16	0			
H	H	CH₃	6-OBs	16	0	——9.0[h]——		3.7
H	CH₃	CH₃	12-OBs	12	0	13.1	1.8	3.4
CH₃	CH₃	CH₃	18-OBs[i]	16	0-1.9[j]	4.5	3.7	3.5

(Products, %[b])

[a] In buffered acetic acid at 40–55°. [b] Based on recovered products = 100%. [c] Reference 3. [d] Nonconjugated allene may isomerize to conjugated allene upon glpc. [e] Reexamination of the uv spectrum of this component indicates that it may contain a small amount (<1% of the total products) of a conjugated triene. [f] Cf. ref 10. [g] Cf. ref 11. [h] May be a mixture of cis and trans isomers, see Results section. [i] Plus ~4% of four other unidentified hydrocarbons, any or all of which may be acyclic. [j] Upper limit represents the amount of the most abundant unidentified hydrocarbon, cf. eq 5.

amounts of 3-alkylidene-2,2-dimethylcyclobutyl acetates which are formed from **6-, 12-,** and **18-OBs** probably result from the further rearrangement of **53** via the tertiary cyclopropylcarbinyl-type cation **54**, viz., Scheme II.

Scheme II

$53 \longrightarrow R_3'R_5C \overset{CH_3}{=} \diamondsuit \overset{+}{\underset{H_3C}{C}} \overset{CH_3}{\diagup} \longrightarrow R_3'R_5 \overset{+}{=} \diamondsuit{-}CH_3$
$\qquad\qquad$ **54** $\qquad\qquad\qquad$ **55**
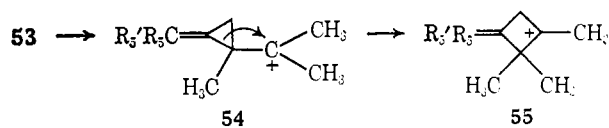
(22) When $R_2 = R_2'$ and R_1 is not hydrogen, when R_2 is not identical with R_2', or perhaps in some cases when R_5 is not identical with R_5', diastereomeric intermediates are possible. We have neglected this consideration in Scheme I and throughout the discussion which follows since we have no data pertinent to this question, but cf. Scheme IV and ref 4 and 14.
(23) Since the reactivity of a homoallenic neopentyl derivative is relatively insensitive to the nucleophilicity of the medium,[3] the "unrearranged" product observed in the case of **11-, 13-,** or **14-OTs** (Table I) must arise from the intermediate **49** (path A) rather than from direct displacement by solvent on the starting material.
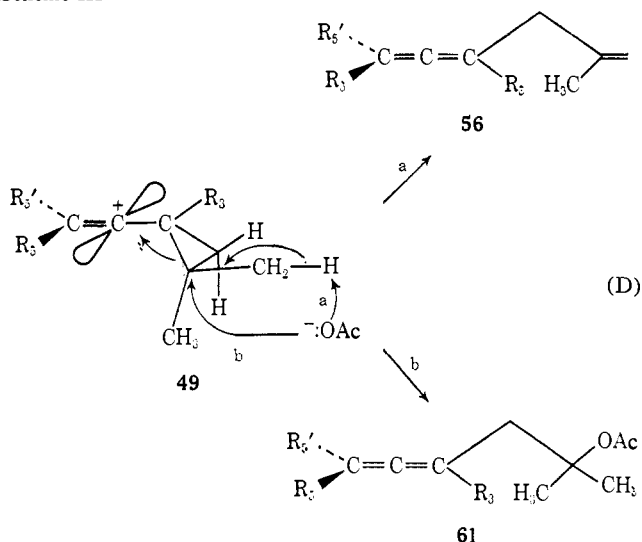
nonconjugated allenes (**56**), conjugated allenes (**57**), trans-conjugated trienes (**58**), cis-conjugated trienes (**59**), and cross-conjugated trienes (**60**); cf. Table II.

Although the allenic trienes and the allenic acetate **61**, which constitute the major products in each of the neopentyl-type arenesulfonates, could come from the tertiary allenic cation **50**,[3] the preponderance of nonconjugated-type olefin **56** in each case leads us to suspect that some or all of these allenic products may actually be formed by direct attack of acetate on the gem-dimethyl cyclopropylcarbinyl-type vinyl cation **49** (path D), viz.,[24] Scheme III.
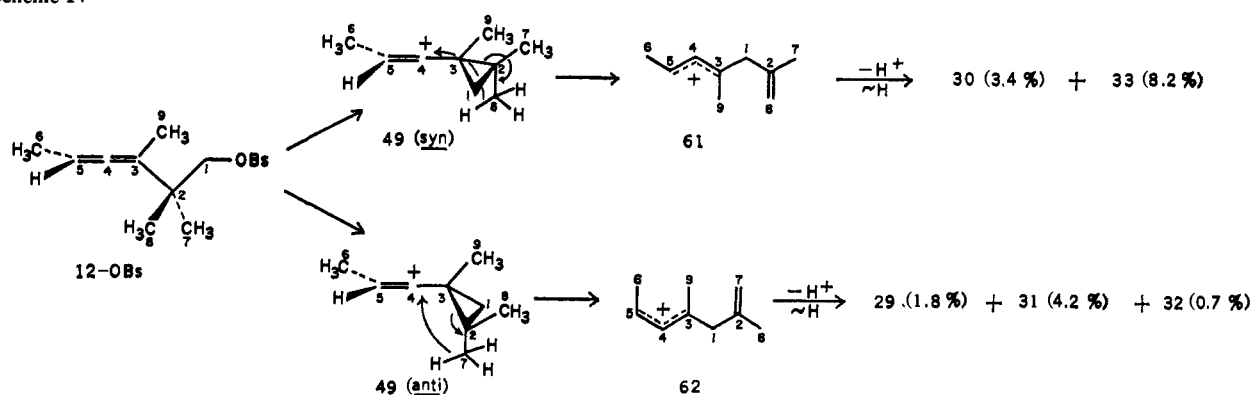
When R_3 is methyl, the allenic trienes are accompanied by appreciable amounts of several nonallenic trienes, a substantial fraction of which are of the less stable "cross-conjugated" variety **60** (Table II). We suggest that the source of these nonallenic trienes in each case may be a nonconjugated hexadienyl cation(s)

(24) A similar suggestion has recently been made to account for some of the products observed in the deamination of some 2-aminocaranes, cf. W. Cocker, D. P. Hanna, and P. V. R. Shannon, Tetrahedron Lett., 4217 (1968).
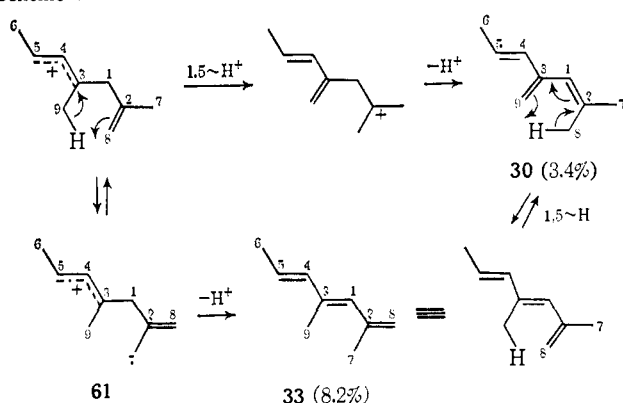
Scheme III

56

49

(D)

61

Scheme IV

12-OBs

49 (syn)

61

(E)

30 (3.4 %) + 33 (8.2 %)

49 (anti)

62

29 (1.8 %) + 31 (4.2 %) + 32 (0.7 %)

Scheme V

30 (3.4%)

61

33 (8.2%)

produced from the *gem*-dimethyl-substituted, cyclo-propylcarbinyl-type vinyl cation **49** by an unusual 1,4-hydride shift (path E) which is competitive with paths A and B. This transformation is illustrated in the case of 2,2,3-trimethyl-3,4-hexadienyl *p*-bromobenzene-sulfonate (**12-OBs**) in Scheme IV.[25] Similar transformations may be pictured for **6**- and **18-OBs**. In each case all of the observed nonallenic trienes may be derived from the appropriate nonconjugated hexadienyl cation(s), *e.g.*, **61** and **62** in the case of **12-OBs**, by a 1,5 intramolecular proton shift and/or proton loss followed in some instances by a 1,5 (or 1,7) sigmatropic hydrogen

(25) The initial ring opening is pictured as stereospecific, *e.g.*, *syn*-**49** to **61**, *anti*-**49** to **62**, because it would appear from models that the rearranging vinyl cation in each case would be well on its way to becoming allylic by the time the transition state is reached.

shift,[26] as illustrated (Scheme V) in the particular case of **30** and **33**. Similar sigmatropic shifts are known to occur readily in other *cis*-dienes and trienes[27] and may take place here during the isolation and analysis. The effect of the methyl group at C-3 is apparently to stabilize developing positive charge at this position during the initial 1,4-hydride migration (Scheme IV) since no nonallenic trienes are observed in its absence. Experiments are planned to test this hypothesis.

Experimental Section[28]

(26) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 2511 (1965).

(27) (a) J. Wolinsky, B. Cholar, and M. D. Baird, *ibid.*, **84**, 2775 (1962), and references cited therein; (b) A. Verloop, A. C. Koevoet, and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **76**, 689 (1957).

(28) Microanalyses were performed by either Bernhardt Mikroanalitishes Laboratorium, Germany, or Galbraith Laboratories, Inc., Knoxville, Tenn. The infrared spectra were determined on a Perkin-Elmer grating spectrophotometer, Model 337, the nuclear magnetic resonance spectra at ambient probe temperature in carbon tetrachloride using a Varian A-60 spectrometer equipped with a Model V-6058A spin decoupler with tetramethylsilane (δ = 0.00) and chloroform (δ = 7.31) as internal standards and the ultraviolet spectra on a Perkin-Elmer ultraviolet–visible spectrophotometer, Model 202. The gas–liquid partition chromatographic (glpc) analyses were carried out on an F & M Model 500 linear temperature programmed gas chromatograph using a 0.25 in. × 16 ft coiled copper tube packed with 20% Carbowax 20M on 100–140 mesh Gas-Chrom S.

as noted below, their relative amounts were independent of the time of reaction.

Products from the Acetolysis of 2,2,3-Trimethyl-3,4-pentadien-1-yl p-Bromobenzenesulfonate (6-OBs) at 55°. Seven components were evident. They were identified as follows.[8]

The **first component** had a retention time of 6.0 min: relative abundance, 16%; ir (CCl$_4$) 3070, 3050 (=CH$_2$), 1965 (>C=C=C<), 1655 (>C=C<), 1450, 1385 (CH$_2$, CH$_3$), 893, 847 cm^{-1} (=CH$_2$); uv (isooctane)[29] [mμ (ϵ)] 213.6 ($\approx$1880), 223.0 ($\approx$770), 254.0 ($\approx$130); nmr (CCl$_4$) δ 4.68 (broad s, 2 =CHH) superimposed on a 1:2:2:1 (?) q at 4.47 (J = 3 Hz, 2 H_2C=C=C(CH$_3$)-), 2.01 (broad s, 2 =C(-)CH$_2$C(-)=), 1.70 (a very slightly perturbed s, 3 =C(-)CH$_3$) superimposed on a 1:2:1 (?) t at 1.54 (J = 3.0 Hz, 3 H$_2$C=C=C-(CH$_3$)-).

These data, together with the absence of gem-dimethyl frequencies in the ir and nmr and conjugated double-bond bands in the uv, clearly indicate that of the 17 possible isomeric, dimethyl-substituted nonconjugated allenic hexatrienes this can only be 2,4-dimethyl-1,4,5-hexatriene (**21**).

The **second component** had a retention time of 8.6 min; relative abundance, 9.0%; ir (CCl$_4$) 3080, 3020 (=CH$_2$, =CH-), 1640, 1600[30] (conj >C=C<), 1445, 1385 (CH$_3$), 997, 900, 842 cm^{-1} (CH=CH$_2$, >C=CH$_2$, >C=CH-); uv (isooctane)[29] [mμ (ϵ)] 211.5 ($\approx$14,800), 246.5 sh ($\approx$30,000), 256.0 ($\approx$35,000), 264.5 ($\approx$34,000), 276.0 sh ($\approx$23,000); nmr (CCl$_4$) δ 6.84 (a 1:1:1:1 q,[31] J_{ac} = 17 Hz, J_{bc} = 11 Hz, 1 H$_a$H$_b$C=CH$_c$C(-)=), 5.70 (broad s, 1 >C=CHC(-)-), 5.3-4.7 (m due apparently to 4 H_aH$_b$C=CH$_c$- + -C(-)=CHH), 1.86 (s superimposed on a s at 1.83 due apparently to 6 -C(CH$_3$)=C(-)- + =C(-)C(CH$_3$)=).

These data, together with the absence of frequencies attributable to allene, gem-dimethyl, or methylene[32] groups, clearly rule out all

A   B   C   D   E   F
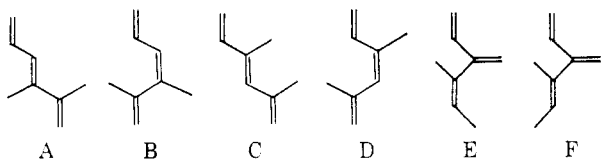
cyclic structures and all but six (A-F) of the 76 possible isomeric dimethyl-substituted hexatrienes and methylidenepentadienes.[32] The two methylidenepentadienes E and F may be excluded on the basis of the strong double-bond (>C=C<) stretch at 1600 cm^{-1}, which is probably too low for a cross-conjugated triene, and the high intensity absorptions at 246, 256, and 264 mμ in the uv.[30,33] Since the nmr spectrum of this component shows the interior vinyl hydrogen, vide supra, as a broad singlet, we have assigned the structure C or D, e.g., 2,4-dimethyl-trans- or -cis-1,3,5-hexatriene to this component (**22**).

The **third component** had a retention time of 10.5 min; relative abundance, 3.7%; ir (CCl$_4$) 3080, 3010 (=CH$_2$, =CH-), 1640, 1620 (conj >C=C<),[30] 1450 (CH$_3$), 1390, 1380, 1360 (>C(CH$_3$)$_2$[34] + CH$_3$), 983 (CH$_2$=CH), 897 (>C=CH$_2$), 840 (?) cm^{-1} (>C=CH); uv (isooctane)[29] [mμ (ϵ)] 214.5 ($\approx$22,900), 231.5 ($\approx$22,500), 247.0 sh ($\approx$20,800), 256.0 ($\approx$24,900), 265.0 ($\approx$25,200), 275.0 (20,500); nmr (CCl$_4$) δ 6.24 (1:1:1:1 q,[31] J_{ac} = 18 Hz, J_{bc} = 10 Hz, 1 H$_a$H$_b$C=CH$_c$C(-)=), 5.77 (broad s, 1 =C(-)CH=C<), 5.3-4.7 (m

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(29) Because of the small quantity of olefin available for study, the absolute magnitudes of these extinction coefficients must be considered approximate although their relative values are precise.

(30) (a) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, pp 24-25; (b) M. Bertrand, Y. Pasternak, J. C. Traynard, J. Le Gras, and A. Guillemonat, *Ann. Fac. Sci. Marselle*, **35**, 85 (1964); cf. p 106.

(31) We recognize that this resonance is a portion of a more complex ABX (or ABC) system and hence should not be subject to a simple intuitive interpretation. In fact, however, a simple analysis seems to provide a reasonably satisfactory interpretation of the observed multiplicity in this case and has been included for this reason; cf. L. M. Jackman "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Oxford. 1959, pp 90-92.

(32) We use the term "methylene" here to mean a carbon bound to two hydrogens and two other carbons, e.g., -CH$_2$-, and "methylidene" to indicate a carbon bound to two hydrogens and by a double bond to another carbon, e.g., =CH$_2$.

(33) T. S. Sorensen, *Can. J. Chem.*, **42**, 2781 (1964).

(34) In contrast to the report of M. Horak and J. Pliva, *Collect. Czech. Chem. Commun.*, **25**, 1679 (1960), we find that an acyclic isopropylidene ((CH$_3$)$_2$C=) or isobutenylidene ((CH$_3$)$_2$C=C=) group usually exhibits a poorly resolved doublet at $\sim$1375 cm^{-1} due to in-plane CH$_3$-C bending.

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due apparently to 4 H_aH$_b$C=CH$_c$- + >C=CHH), 1.87 (slightly perturbed s, 6 =C(CH$_3$)CH$_3$).

The absence of an allene frequency and the presence of the conjugated double-bond absorptions in the ir together with the four terminal vinyl hydrogens and two nonequivalent vinyl-methyl resonances in the nmr clearly indicate a gem-dimethyl-substituted, nonallenic triene. The uv spectrum is quite complex and changes with time. The two fairly intense absorptions at 214.5 and 231 mμ appeared to be those of a cross-conjugated triene[35] while the slightly more intense maxima at 247, 256, 265, and 275 mμ, which become stronger on standing, resemble those of a conjugated triene.[33] After a solution of this component in isooctane has been allowed to stand at 0° for several weeks it no longer exhibits the maxima at 214.5 and 231 mμ. Clearly component three is a mixture. We believe that it initially consists of 2-methyl-4-methylidene-2,5-hexadiene[32] (**23**) predominantly, the only one of the 13 possible isomeric dimethyl-substituted methylidenepentadienes consonant with the spectral data, but that this compound is contaminated with and slowly isomerizes to 2,4-dimethyl-trans-1,3,5-hexatriene during the work-up and isolation. The nmr spectrum is equally compatible with either of these structures.

The **fourth component** had a retention time of 37.3 min; relative abundance, 0.6%; ir (CCl$_4$) 3075, 3020 (=CH$_2$), 1740 (>C=O), 1695, 890 (>C=CH$_2$), 1460 (CH$_3$), 1440 (>CH$_2$), 1390, 1375 (>C-(CH$_3$)$_2$), 1241 (CH$_3$COO), 1225 cm^{-1} (COO); uv (isooctane)[29] [mμ (ϵ)] 211.5 ($\approx$360), 227.0 sh ($\approx$160), 257.0 ($\approx$60), nmr (CCl$_4$) δ 5.03 (broad s, 1 HHC=C<), 4.72 (broad s, 1 HHC=C<), 2.16 (broad s, 2 >CHH), 1.95 (s, 3 -OCOCH$_3$), 1.48 (s, 3 >C(CH$_3$)O-), 1.20 (s, 3 >C(CH$_3$)CH$_3$), 1.04 (s, 3 >C(CH$_3$)CH$_3$).

The **fifth component** had a retention time of 41.3 min; relative abundance, 2.0%; ir (CCl$_4$) 3065 (=CH$_2$), 1740 (>C=O), 1685, 880 (>C=CH$_2$), 1470 (CH$_3$), 1435 (>CH$_2$), 1380, 1370 (>C(CH$_3$)$_2$), 1250 cm^{-1} (CH$_3$COO-); uv (isooctane)[29] [mμ (ϵ)] 214.0 ($\approx$300), 227.0 sh ($\approx$160), 265.0 ($\approx$17), nmr (CCl$_4$) δ 4.70 (perturbed s, 2 HHC=C-), 2.76 (center of AB q, δ_{H_a} = 3.00, δ_{H_b} = 2.54, J_{ab} = 15 Hz, 2 H_aH$_b$C<), 1.93 (s, 3 -OCOCH$_3$), 1.42 (3 >C(CH$_3$)O-), 1.13 (s, 6 >C(CH$_3$)CH$_3$).

The **sixth component** had a retention time of 59.3 min; relative abundance, 2.0%; ir (CCl$_4$) 3025 weak (=CH), 1700 sh (>C=C<), 1745 (>C=O), 1460 (CH$_3$), 1445 (CH$_2$), 1380, 1365 (>C(CH$_3$)$_2$), 1233-1220 (CH$_3$COO-), $\sim$895 weak cm^{-1} (>C=CH$_2$); uv (isooctane)[29] [mμ (ϵ)] 214.5 ($\approx$540), 225.5 sh ($\approx$240), 264.5 ($\approx$80); nmr (CCl$_4$) δ 4.38 (broad s, 2 HHC=C<), 2.05 (broad s, 2 >CHH) superimposed on a s at 1.98 (3 -OCOCH_3), 1.57 (broad s, 3 >C-(CH$_3$)O-), 1.10 (slightly perturbed s, 6 >C(CH$_3$)CH$_3$).

It is evident from their ir spectra that these three components are nonallenic unsaturated acetates; from their uv spectra that they are not dienes. The absence of any enol-oxygen-type (=CO-) stretches in the ir and resonances in the nmr for hydrogens bonded to oxygen-bearing carbons indicates that none of these esters is an enol acetate, by inference that none contains a cyclopropane ring, but that each is a tertiary acetate. Thus these three minor esters must be the methylidene-gem-dimethylcyclobutyl acetates[32] **17-**, **19-**, and **20-OAc**, illustrated below in each of their two possible conformations. If the conformational preference of this ring


a ⇌ b
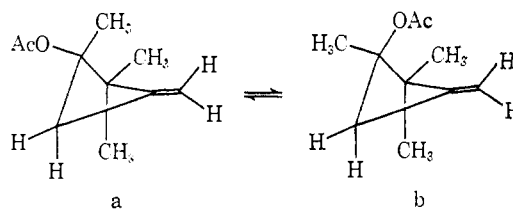
17-OAc

system is similar to that of cyclohexane, e.g., methyl prefers an equatorial position more strongly than does acetoxy,[36] then conformer a will be the more stable in each case.

Although it is not possible to make a completely unambiguous structural assignment on this basis, we have used the nmr data, summarized in Table III, to tentatively assign their structures.

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(35) A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.*, **77**, 81 (1955).

(36) Cf. E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 236, and references cited therein.
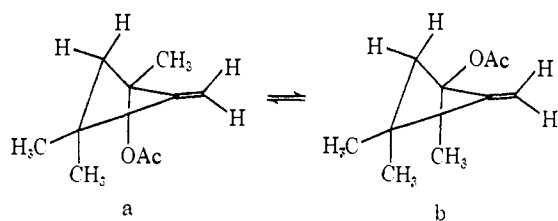
19-OAc
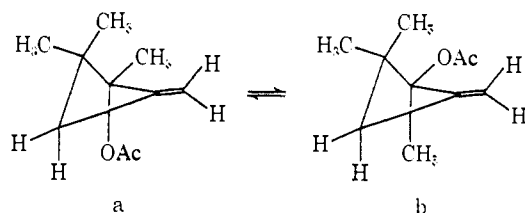
20-OAc

To the fifth component, which has the lowest field methylene[32] hydrogens, presumably because they are not only allylic[37] but β to the acetoxy group, and the highest field acetoxy and methylol methyls (OCOCH₃ and >C(CH₃)O, respectively), because in one conformer each lies partially in the region of positive anisotropy above the double bond, we have assigned the structure 17-OAc. We attribute structure 19-OAc to the sixth component for the nmr spectrum of this ester exhibits the highest field methylidene[32] and

Table III. Observed Proton Chemical Shifts of the Methylidene-gem-dimethylcyclobutyl Acetates from the Acetolysis of 6-OBs[a]

	Component		
	4th (20-OAc)	5th (17-OAc)	6th (19-OAc)
=CHH	5.03 (d), 4.72 (d)	4.70	4.38
>CHH	2.16	2.76 (q)	2.05
-OCO(CH₃)	1.95	1.93	1.98
>C(CH₃)O-	1.48	1.42	1.57
>C(CH₃)₂	1.20, 1.04	1.13	1.10

[a] In parts per million downfield relative to tetramethylsilane = 0.00.

gem-dimethyl resonances,[34] the latter because in each of the conformers one of the methyls is deshielded by the double bond while in this isomer neither is vicinal to the acetoxy group, and the lowest field methylol-methyl resonance. Presumably conformer a with the equatorial methylol methyl is considerably more stable in this case and the methyl is deshielded because in this conformer it is nearly coplanar with the carbons of the double bond. Also in the more stable conformer the vinyl hydrogens are shielded by the carbonyl of the acetate and appear at a higher than normal field while the acetoxy methyl is shifted slightly to lower field by the carbon-carbon double bond. Structure 20-OAc is assigned to the fourth component. In this isomer the hydrogens of the methyl group which is cis to the acetoxy, and to a lesser extent that of the cis-vinyl, are shielded by the carbonyl and appear at a higher field. The remaining gem-methyl is slightly deshielded by the double bond.

The seventh component had a retention time of 73 min; relative abundance, 66%; ir (CCl₄) 1960 (>C=C=C<), 1740 (>C=O), 1475 (CH₂), 1450 (CH₃), 1390, 1375 (>C(CH₃)₂), 1235–1260 (CH₃-COO-), 843 cm⁻¹ (CH₂=⁼C=C(-)-); uv (isooctane) [mμ (ε)] 212.5 (≈470), 226.5 sh (≈266); nmr (CCl₄) δ 4.42 (complex, m, 2 H₂C=C=C(CH₃)-), 2.38 (perturbed t, 2 H₂C=C=C(-)CH₂C<), 1.89 (s, 3 -OCOCH₃), 1.70 (perturbed t, 3 H₂C=C=C(CH₃)-), 1.43 (s, 6 -C(CH₃)₂O-).

(37) I. Fleming and D. H. Williams, Tetrahedron, 23, 2747 (1967).

Anal. Calcd for C₁₀H₁₆O₂: C, 71.39; H, 9.58. Found: C, 71.34; H, 9.52.

The absence of a resonance attributable to a hydrogen bonded to an oxygen-adjacent carbon (>C(H)O-) indicates that this acetate is tertiary (≫COAc). Hence this component can only be the rearranged acyclic ester, 2,4-dimethyl-4,5-hexadien-2-yl acetate (16-OAc).

Products from the Acetolysis of 2,2-Dimethyl-3,4-hexadien-1-yl p-Bromobenzenesulfonate (9-OBs) at 55°. Three components were evident. They were identified as follows.[5]

The first component had a retention time of 7.5 min; relative abundance, 21%; ir (CCl₄) 3075 (=CH₂), 1975 (>C=C=C<), 1660, 890 cm⁻¹ (>C=CH₂); uv (isooctane) [mμ (ε)] 209.5 (≈1460); nmr (CCl₄) δ 4.90 (m, 2 CH₃CH=C=CHCHH-), 4.64 (broad s, 2 >C=CHH), 2.62 (perturbed t, 2 -CHₐ=C=CHᵦCHHC(-)=) which collapses to a broad singlet when irradiated at −136 Hz (e.g., when decoupled from the nearly equivalent Hₐ and Hᵦ), 1.72 (s, 3 =C(-)CH₃) superimposed on a t(?) at 1.61 (3 CH₃CH=C=CH-).

We conclude that this component is 2-methyl-1,4,5-heptatriene[4] (24).

The second component had a retention time of 16.4 min; relative abundance, 6.1%; ir (CCl₄) 3080 (>C=CH₂), 3020 (>C=CH), 1945 (>C=C=C<), 1650, 1625 (>C=C<), 1410, 1385 (=C(CH₃)₂), 872 cm⁻¹ (CH=C=CH); uv (isooctane)[29] [mμ (ε)] 225.5 (≈16,000), 236.5 (≈17,000), 241.5 sh (≈16,500), 262.0 (≈9000), 273.0 (≈6900); nmr (CCl₄) δ 6.3–5.4 (complex m, 2 CH₃CH=C=CH—CH=), 5.4–4.7 (complex m, 1 CH₃CH=C=CH-), 2.2–1.2 (complex m, 3 CH₃CH=C=CH-) superimposed upon singlets at 1.72 and 1.67 (6 -CH=C(CH₃)CH₃).

We conclude that this component is 2-methyl-2,4,5-heptatriene[4] (25).

The third component had a retention time of 60 min; relative abundance, 73%; ir (CCl₄) 3010 (>C=CH), 1965 (>C=C=C<), 1740 (>C=O), 1475 (CH₂), 1385, 1375 (>C(CH₃)₂), 1240 (OCOCH₃), 873 cm⁻¹ (HC=C=CH); uv (isooctane) [mμ (ε)] 210 (≈740), 267 (≈150), 273 (≈130); nmr (CCl₄) δ 5.16–4.71 (complex m, 2 CH₃CH=C=CHCHH-) which collapses to a broad perturbed p (?) when irradiated at +197 or +153 Hz (i.e., when decoupled from the methyl or methylene hydrogens, respectively), 2.37 (perturbed q, 2 -CHₐ=C=CHᵦCHHC<[31]) which collapses to a broad perturbed s when irradiated at −153 Hz (i.e., when decoupled from the nearly equivalent Hₐ and Hᵦ), 1.87 (s, 3 -OCOCH₃), 1.61 (perturbed q, 3 CH₃CHₐ=C=CHᵦCHH-) which collapses to a broad perturbed s (?) when irradiated at −197 Hz (i.e., when decoupled from the nearly equivalent Hₐ and Hᵦ), 1.40 (s, 6 -C(CH₃)(CH₃)O-).

Anal. Calcd for C₁₀H₁₆O₂: C, 71.39; H, 9.59. Found: C, 71.34; H, 9.52.

We conclude that this component is 2-methyl-4,5-heptadien-2-yl acetate (26-OAc).

Products from the Acetolysis of 2,2,3-Trimethyl-3,4-hexadien-1-yl p-Bromobenzenesulfonate (12-OBs) at 40°. Eleven components were present. They were identified as follows.[5]

The first component had a retention time of 10.2 min; relative abundance, 2.4%; ir (CCl₄) 3085, 3060, 3030 (>C=CH), 1650 (>C=C<), 1490 (CH₂), 1385, 1370 (>C(CH₃)₂), 870 (>C=CH₂), 830 cm⁻¹ (>C=CH); uv (isooctane)[29] [mμ (ε)] 211.0 (≈1950), 238.0 sh (≈4300), 248.0 ? (≈5200), 255.0 sh (≈4200); nmr (CCl₄) δ 5.6 (broad m (?), 1 CH₃CH=C<), 4.78 (perturbed s, 1 >C=CHH), 4.43 (perturbed s, 1 >C=CHH), 2.29 (broad s, 2 ≫CCH₂-C(-)=), 1.57 (broad perturbed 1:1 d, J ≈ 7 Hz, 3 H₃CCH=C<), 1.17 (s, 6 >C(CH₃)₂).

We conclude that this component is a 3,3- or 4,4-dimethyl-2-methylidene-1-ethylidenecyclobutane (27) of undetermined stereochemistry.

The second component had a retention time of 12.4 min; relative abundance, 12%; ir (CCl₄) 3070 (=CH₂), 1970 (>C=C=C<), 1655 (>C=C<), 889 (>C=CH₂), 1475 sh, 1450, 1380 cm⁻¹ (>CH₂, CH₃); uv (isooctane) [mμ (ε)] 213.5 (≈1950), nmr (CCl₄) δ 4.8 (broad m (?), 1 CH₃CH=C=C(CH₃)-) superimposed on a broad s at 4.65 (2 -C(-)=CHH), 2.63 (slightly perturbed s, 2 =C(-)CHHC(-)=), 1.68 (s (?), 3 -(CH₃)C=) superimposed upon a 1:1 d at 1.60 (J ≈ 7 Hz, 3 H₃CCH=C=C(-)-) and also upon a 1:1 d at 1.57 (J ≈ 3 Hz, 3 -CH=C=C(CH₃)-).

Anal. Calcd for C₉H₁₄: C, 88.45; H, 11.55. Found: C, 88.55; H, 11.54.

We conclude that this component is 2,4-dimethyl-1,4,5-heptatriene (28).

The **third component** had a retention time of 17.6 min; relative abundance, 1.8%; ir (CCl₄) 3065, 3020 (>C=CH), 1640–1645 (conj >C=C<), 1385, 1380 (>C(CH₃)₂), 995, 895 cm⁻¹ (HC=CH₂); uv (isooctane)²⁹ [mμ (ε)] 213.5 (≈11,600), 247.0 (≈14,500); nmr (CCl₄) δ 6.8–5.5 (a complex m, 3 CH₂=CHCH=C(CH₃)CH=C<), 4.98 (complex m, 2 HHC=CHCH=), 1.80 (perturbed broad s, 6 -CH=C(CH₃)CH₃), 1.57 (slightly perturbed d (?), J ≈ 2 Hz, 3 -CH=C(CH₃)-).

We believe that this component is 4,6-dimethyl-*cis*-1,3,5-heptatriene (**29**).

The **fourth component** had a retention time of 19.6 min; relative abundance, 3.4%; ir (CCl₄) 3080, 3005 (>C=CH), 1652, 1600 (conj >C=C<),³⁰ 1452, 1380 (CH₃), 965 (*trans* -CH=CH-), 890 cm⁻¹ (>C=CH₂); uv (isooctane)²⁹ [mμ (ε)] 216.0 (≈14,700), 221.5 (≈15,000), 231.5 (≈12,900); nmr (CCl₄) δ 6.2–5.5 (complex m, 3 H₃CCH=CHC(=CH₂)CH=C<), 4.92 (broad s, 1 >C=CHH), 4.67 (broad s, 1 >C=CHH), 1.80, 1.67 (singlets superimposed on a doublet (?), J = 7 Hz, 9 (CH₃)HC=CH- + -CH=C(CH₃)CH₃).

We believe that this component is probably 2-methyl-4-methylidene-2,5-heptadiene (**30**).

The **fifth component** had a retention time of 26.5 min; relative abundance, 4.2%; ir (CCl₄) 3075, 3027 (>C=CH), 1630, 1610 (conj triene),³⁰ 1450, 1380 (CH₃), 970, 960 (>C=CH), 895 cm⁻¹ (>C=CH₂); uv (isooctane)²⁹ [mμ (ε)] 213.0 (≈21,600), 249.0 sh (≈34,400), 258.5 (≈37,700), 268.5 (≈37,000), 279.0 sh (≈24,200); nmr (CCl₄) δ 6.53 (broad d, J ≈ 15 Hz, 1 -CH=CHC(-)=), 5.59 (m, 1 H₃CCH=CH-) superimposed upon a broad s at 5.55 (1 >C=CHC(-)=), 4.87 (broad s, 1 -C(-)=CHH), 4.71 (broad s, 1 -C(-)=CHH), 1.82 (broad s, 6 =CHC(CH₃)=CH- + =CHC(CH₃)=C<) superimposed upon a d at 1.77 (J ≈ 6 Hz, 3 H₃C-CH=C<).

Anal. Calcd for C₉H₁₄: C, 88.45; H, 11.55. Found: C, 88.49; H, 11.63.

We believe that this component is a conjugated triene, probably 2,4-dimethyl-*trans,cis*-1,3,5-heptatriene (**31**).³³

The **sixth component** had a retention time of 31.8 min; relative abundance, 0.7%; ir (CCl₄) 3080, 3020 (>C=CH), 1635, 1600 (conj triene),³⁰ 1450 (CH₃), 1385, 1375 (>C(CH₃)₂), 980, 900 (CH=CH₂), 790–760 cm⁻¹ (*cis* -CH=CH-); uv (isooctane) [mμ (ε)] 211.0 (≈8100), 258.5 (≈35,200), 266.0 (≈33,900), 278.0 (≈21,000).

From the similarity of the ir and uv with those of the known³³ 4,6-dimethyl-*trans*-1,3,5-heptatriene, we conclude that the probable structure of this component is **32**.

The **seventh component** had a retention time of 36.6 min; relative abundance, 8.2%; ir (CCl₄) 3080, 3020 (>C=CH), 1630 (conj >C=C<), 1455 (CH₃), 1400, 1380 (>C(CH₃)₂), 958 (*trans* -CH=CH-), 890 cm⁻¹ (=CH₂); uv (isooctane)²⁹ [mμ (ε)] 211.5 (≈7000), 248.5 sh (≈22,000), 259 (≈27,500), 268.0 (≈27,100), 269.0 sh (≈18,000); nmr (CCl₄) δ 6.2–5.3 (complex m, 3 CH(-)=CHC(-)=CH-), 4.90 (broad s, 1 >C=CHH), 4.73 (broad s, 1 >C=CHH), 1.88 (s, 3 =CHC(CH₃)=CH- ?) superimposed on a s at 1.86 (3 =CHC(CH₃)=CH₂ ?) and a d at ~1.8 (J ~ 7 Hz, 3 CH₃-CH=).

Anal. Calcd for C₉H₁₄: C, 88.45; H, 11.55. Found: C, 88.40; H, 11.55.

We believe that this component is 2,4-dimethyl-*trans,trans*-1,3,5-heptatriene (**33**).

The **eighth component** had a retention time of 66.7 min; relative abundance, 8.6%; ir (CCl₄) 3010 (>C=CH), 1730 (>C=O), 1450, 1470 (>CH₂, CH₃), 1375, 1380 sh (>C(CH₃)₂), 1235 (OCOCH₃), 838 cm⁻¹ (>C=CH); uv (isooctane) [mμ (ε)] 213.5 (≈1225), 243.0 (≈700); nmr (CCl₄) δ 5.27 (broad q, J ≈ 7 Hz, 1 CH₃CH=C<), 2.01 (broad s, 2 >CHH) superimposed upon an s at 1.98 (3 -OCOCH₃), 1.58 (broad perturbed s, 3 -C(-)(CH₃)OCO-), 1.25 (d, J ≈ 7 Hz, 3 CH₃CH=), 1.07 (s, 6 >C(CH₃)CH₃).

Anal. Calcd for C₁₁H₁₈O₂: C, 72.49; H, 9.96. Found: C, 72.36; H, 10.37.

We believe that this component is an ethylidenecyclobutyl acetate, probably a 1,3,3-trimethyl-2-ethylidenecyclobutyl acetate (**34**-OAc).

The **ninth component** had a retention time of 87 min; relative abundance, 0.8%; ir (CCl₄) 3080, 3035 (>C=CH), 1740 (>C=O), 1450, broad (CH₃, >CH₂), 1390, 1380 (>C(CH₃)₂), 1245 cm⁻¹ (OCOCH₃). The infrared spectrum shows that this material is a nonallenic unsaturated *gem*-dimethyl acetate. Excluding geometric isomers there are three possible ethylidene-*gem*-dimethylcyclobutyl acetates, this is probably one of the 1,4,4-trimethyl-2-ethylidenecyclobutyl acetates (**35**-OAc).

The **tenth component** had a retention time of 100 min; relative abundance, 2.1%; ir (CCl₄) 3040, 3020 (>C=CH), 1740 (>C=O),

1475, 1465, 1450, 1440 (CH₃, >CH₂), 1390, 1380 (>C(CH₃)₂), 1250 (OCOCH₃), 842 cm⁻¹ (>C=CH); uv (isooctane) [mμ (ε)] 212.0 (≈420); nmr (CCl₄) δ 5.1 (broad m, 1 CH₃CH=C(-)CHH-), ~2.82, 2.62 (broad AB quartet, J ≈ 15 Hz, 2 >CHH), 1.92 (s, 3 -OCOCH₃), 1.49 (perturbed broad d (?), J ≈ 7 Hz, 3 CH₃CH=) superimposed on an s at 1.40 (3 >C(CH₃)O-), 1.09 (slightly perturbed s, 6 >C(CH₃)CH₃).

We believe that this component is one of the ethylidenecyclobutyl acetates, probably 1,2,2-trimethyl-3-ethylidenecyclobutyl acetate (**36**-OAc).

The **eleventh component** had a retention time of 156 min; relative abundance, 60%; ir (CCl₄) 3015 sh (>C=CH), 1965 (>C=C=C<), 1745 (>C=O), 1470, 1450 (>CH₂, CH₃), 1385, 1375 (>C(CH₃)₂), 1250 (OCOCH₃), 840 cm⁻¹ (HC=C=C<); uv (isooctane) [mμ (ε)] 215.5 (≈1625), 229.0 (≈1100), 285.0 (≈23); nmr (CCl₄) δ 4.84 (broad m, 1 H₃CCH=C=C(CH₃)-), 2.39 (s, 1 =C-(-)CHHC<), 2.34 (s, 1 =C(-)CHHC<), 1.89 (s, 3 -OCOCH₃), 1.68 (1:1 d, J ≈ 3 Hz, 3 -CH=C=C(CH₃)-) superimposed upon a 1:1 d at 1.60 (J ≈ 7 Hz, 3 CH₃CH=C=C(-)-), 1.44 (s, 6 >C(CH₃)CH₃).

Anal. Calcd for C₁₁H₁₈O₂: C, 72.49; H, 9.96. Found: C, 72.68; H, 10.38.

We conclude that this component is 2,4-dimethyl-4,5-heptadien-2-yl acetate (**37**-OAc).

The composition of the acetates but not of the hydrocarbons is invariant with time.

Products from the Acetolysis of 2,2,5-Trimethyl-3,4-hexadien-1-yl *p*-Bromobenzenesulfonate (15-OBs) at 40°. The two components which were evident had the following spectral properties.⁸

The **first component** had a retention time of 7.0 min; relative abundance, 16%; ir (CCl₄) 3065 (>C=CH), 1965 (>C=C=C<), 1652 (>C=C<), 1375, 1365 (>C(CH₃)₂), 887 (>C=CH₂), 845 cm⁻¹ (>C=CH); uv (isooctane)²⁹ [mμ (ε)] 211 (≈2140), 238 (≈965); nmr (CCl₄) δ ~5.0 (broad m, 1 (CH₃)₂C=C=CHCH₂-) which collapses to a broad irregular triplet (?) when irradiated at +187 Hz (*i.e.*, when decoupled from the six equivalent methyl hydrogens) superimposed upon a broad s at 4.72 (2 >C=CHH), 2.60 (slightly perturbed d, J ≈ 7 Hz, 2 =CHCH₂C(-)=), 1.79 (broad s (?), 6 (CH₃)₂C=C=CH-), 1.63 (s, 3 -C(CH₃)=).

Anal. Calcd for C₉H₁₄: C, 88.45; H, 11.55. Found: C, 88.25; H, 11.60.

We conclude that this component is 2,6-dimethyl-1,4,5-heptatriene (**38**).

The **second component** had a retention time of 61 min; relative abundance, 84%; ir (CCl₄) 1975 (>C=C=C<), 1740 (>C=O), 1445 (>CH₂), 1390, 1370 (>C(CH₃)₂), 1235 (OCOCH₃), 852 cm⁻¹ (>C=C=CH); uv (isooctane) [mμ (ε)] 210 (≈1100), 240 sh (≈440), 270 (≈150), 285 (≈100); nmr (CCl₄) δ 4.8 (broad m, 1 (CH₃)₂C=C=CHCH₂-), 2.35 (d, J = 7 Hz, 2 =CHCH₂C<), 1.90 (s, 3 -OCOCH₃), 1.68 (perturbed d, J ≈ 2 Hz, 6 (CH₃)₂C=C=CH-), 1.42 (slightly perturbed s, 6 -C(CH₃)₂O-).

Anal. Calcd for C₁₁H₁₈O₂: C, 72.49; H, 9.96. Found: C, 72.32; H, 10.00.

We conclude that this component is 2,6-dimethyl-4,5-heptadien-1-yl acetate (**39**-OAc).

Products from the Acetolysis of 2,2,3,5-Tetramethyl-3,4-hexadien-1-yl *p*-Bromobenzenesulfonate (18-OBs) at 40°. Thirteen components were evident. Their identities were inferred from the following spectral and analytical data.⁸

The **first component** which had a retention time of 3.8 min and a relative abundance of 0.5% was not collected or identified.

The **second component** had a retention time of 4.1 min; relative abundance, 16%; ir (CCl₄) 3075, 3020 (>C=CH), 1980 (>C=C=C<), 1660 (>C=C<), 1455 (>CH₂, CH₃ ?), 1380, 1375 (>C-(CH₃)₂), 890 cm⁻¹ (>C=CH₂); uv (isooctane) [mμ (ε)] 214.5 (≈2500); nmr (CCl₄) δ 4.67 (broad s, 2 >C=CHH), 2.57 (broad s, 2 >CH₂), 1.66 (perturbed s, 6 (CH₃)₂C=C=C<) superimposed on a perturbed s at 1.64 (3 >C=C=C(CH₃)-) and upon a slightly perturbed s at 1.58 (3 -C(CH₃)=CH₂).

We conclude that this component is 2,4,6-trimethyl-1,4,5-heptatriene (**40**).

The **third component** had a retention time of 4.6 min; relative abundance, 6.7%; ir (CCl₄) 3080 (>C=CH₂), 1655, 1605 (>C=C<), 1460 (>CH₂), 1380, 1370 (>C(CH₃)₂), 878 cm⁻¹ (>C=CH₂); uv (isooctane)²⁹ [mμ (ε)] 235.0 sh (≈4600), 243.0 (≈5050), 252.0 (≈3800); nmr (CCl₄) δ 4.63 (broad s, 2 >C=CHH), 2.12 (broad s, 2 -CHH-), 1.88 (slightly perturbed s, 3 >C=C-(CH₃)CH₃), 1.73 (slightly perturbed s, 3 >C=C(CH₃)CH₃), 1.10 (s, 6 > C(CH₃)₂).

We believe that this component is 3,3- or 4,4-dimethyl-1-isopropylidene-2-methylidenecyclobutane[32] (41).

The fourth component had a retention time of 5.2 min; relative abundance 0.8%; and was not collected or identified.

The fifth component which had a retention time of 6.4 min and a relative abundance of 6.2% consisted of three olefins in the ratio of 6:3:1 which were only partially resolved on the 16-ft Carbowax column at 60°. These olefins were not individually collected and identified but the nmr spectrum (CCl_4), determined of the mixture, had signals at δ 5.73 (slightly perturbed s, >C=CHC(-)=CH-), 4.77 (broad perturbed s, (?), -C(-)=CH$_2$), 1.82, 1.75, 1.60 (perturbed singlets, $(CH_3)_2C=CHC(CH_3)=CHC(CH_3)=CH_2$). Weaker, unassigned signals are at δ 4.9, 2.8, 2.64, and 1.66.

We feel that the principal component of this mixture is probably 2,4,6-trimethyl-cis-1,3,5-heptatriene (42).

The sixth component had a retention time of 7.8 min; relative abundance, 3.5%; ir (CCl_4) 3080, 3015 (>C=CH), 1650, 1600 (>C=C<), 1450 (CH$_3$), 1385, 1380 (>C(CH$_3$)$_2$), 889 cm^{-1} (>C=CH$_2$); uv (isooctane)[29] [mμ (ϵ)] 218.5 ($\approx$15,700), 243.0 ($\approx$13,200); nmr (CCl_4) δ 5.64 (broad s, 2 >C=CHC(=)CH=C<), 4.82 (s, 2 >C=CH$_2$), 1.74 (slightly perturbed s, 12 $(CH_3)_2C=C(-)$C(=)C(-)=C(CH$_3$)$_2$).

We conclude that this is the known 2,6-dimethyl-4-methylidene-2,5-heptatriene[32] (43).[33]

The seventh component had a retention time of 8.8 min; relative abundance, 4.5%; ir (CCl_4) 3080, 3020 (>C=CH), 1640 (>C=C<), 1450, 1380 (CH$_3$), 890 cm^{-1} (>C=CH$_2$); uv (isooctane)[29] [mμ (ϵ)] 213 ($\approx$5100), 258 ($\approx$10,100), nmr (CCl_4) δ 5.57 (broad s, 2 >C=CHC(-)=CH-), 4.88 (broad s, 1 -C(-)=CHH), 4.74 (broad s, 1 -C(-)=CHH), 1.83 (slightly perturbed s, 6 $(CH_3)_2$-C=C(-)-), 1.75 (slightly perturbed s, 6 -C(CH$_3$)=C(-)C(CH$_3$)=).

We conclude that this is the known 2,4,6-trimethyl-trans-1,3,5-heptatriene (44).[33]

The eighth component had a retention time of 32.8 min; relative abundance, 60%; ir (CCl_4) 1965 (>C=C=C<), 1730 (>C=O), 1460, 1445 (>CH$_2$, CH$_3$), 1375, 1360 (>C(CH$_3$)$_2$), 1245 cm^{-1} (OCOCH$_3$); uv (isooctane) [mμ (ϵ)] 214.7 ($\approx$1950); nmr (CCl_4) δ 2.35 (s, 2 =C(-)CH$_2$C<), 1.88 (s, 3 -OCOCH$_3$), 1.64 (slightly perturbed s, 9 $(CH_3)_2C=C=C(CH_3)$-) overlapping with a singlet at 1.43 (6 -C(CH$_3$)$_2$O-).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 73.43; H, 10.27. Found: C, 73.18; H, 10.30.

We conclude that this component is 2,4,6-trimethyl-4,5-heptadien-2-yl acetate (45).

The ninth component had a retention time of 36.8 min; relative abundance, 0.7%; ir (CCl_4) 1745 (>C=O), 1450 (CH$_3$), 1390, 1380 (>C(CH$_3$)$_2$), 1255 cm^{-1} (OCOCH$_3$); uv (isooctane)[29] [mμ (ϵ)] 215.0 ($\approx$350).

The tenth component had a retention time of 43.4 min; relative abundance, 0.3%; ir (CCl_4) 1740 (>C=O), 1450 (CH$_3$) 1385, 1370 (>C(CH$_3$)$_2$), 1250 cm^{-1} (OCOCH$_3$); uv (isooctane)[29] [mμ (ϵ)] 215.0 ($\approx$400).

The nmr spectra of the ninth and tenth components could not be determined because of the small amounts available. They are, however, assumed to be two of the three possible gem-dimethyl-isopropylidenemethylcyclobutyl acetates (46- and 47-OAc) because of the similarity of the ir and uv spectra with those of the closely related cyclobutyl acetates, 17-, 19-, 20-, 34-, 35-, and 36-OAc.

The eleventh component had a retention time of 50.8 min; relative abundance, 1.0%; ir (CCl_4) 3080, 3020, 895 (>C=CH- ?), 1740 (>C=O), 1640 (>C=C<), 1450 (CH$_3$), 1390, 1380 (>C-(CH$_3$)$_2$), 1250 cm^{-1} (OCOCH$_3$); uv (isooctane) [mμ (ϵ)] 213.0 ($\approx$800).

The ir and uv spectra suggest that this component may be one or a mixture of the isomeric gem-dimethylisopropenylmethylcyclobutyl acetates (48-OAc) but the evidence is insufficient for a definite structure assignment.

Because of the small amount of sample available to us we were unable to determine the stability of these components under the reaction conditions, but were able to demonstrate that unreacted brosylate, recovered after one half-life had not been isomerized.