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Studies of Benzonorbornene and Derivatives. VI. Peroxide-Induced Decarbonylation of *syn*- and *anti*-Benzonorbornene-7-carboxaldehydes[1,2]

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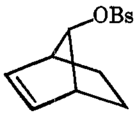
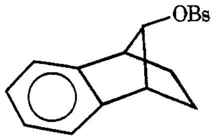
The synthesis of the title aldehydes has been achieved. As a sidelight to the synthesis, a convenient new preparation of benzonorbornen-7-one was developed. The peroxide-induced decarbonylation of the title aldehydes proceeded faster with the anti epimer. Benzonorbornene was the principal product along with uncharacterized resinous material. The faster reaction of the anti epimer was most probably a reflection of its greater chain-transfer ability and *not* a consequence of any pronounced participation in decarbonylation by the π electrons of the aromatic ring. Chain-transfer reactions with chlorine donors served to demonstrate these reaction features. Discussion of the nmr spectra of the aldehydes is also presented.

The ability of the norbornene double bond to participate in the solvolysis of *anti*-7-norbornenyl substrates such as **1** is amply documented.[4] A similar rate effect exists for the benzonorbornenyl analog **2**, though π participation by the aromatic ring is here somewhat less dramatic.[4]

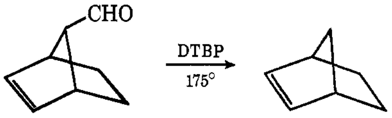


1



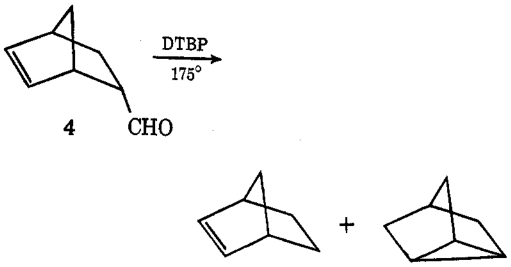
2

In earlier work it was found that a *radical* reaction involving the 7 position in norbornene likewise seemed to be influenced by the double bond.[5] Aldehyde **3** lost carbon monoxide much more readily than its isomer **4** (eq 1 and 2). It was suggested that **3** utilized π participation in the loss of carbon monoxide leading to a symmetrical, delocalized radical species (eq 3). Since that time several claims and counterclaims concerning nonclassicality in 7-norbornenyl and related radicals have appeared.[6]



3

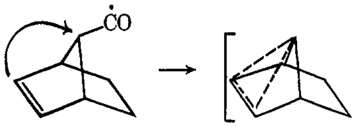
+ CO (80% in 2 hr) (1)



4

+ CO (2)

(14% in 3 hr)



+ CO (3)

The reactions in eq 1 and 2 were disadvantaged because a side reaction leading to polymer cut the yield of monomeric hydrocarbon badly (2.3% from **3**, 8.6% from **4**). It was therefore of interest to prepare the benzo analog of **3**, benzonorbornene-*anti*-7-carboxaldehyde (**5**), and to study its decarbonylation, particularly with regard to its syn epimer **6**. Polymerization would no longer be a problem and the benzo analog otherwise should mirror **3** to an extent comparable to the ionic situation with **1** and **2** mentioned above. So perhaps a more meaningful search for π participation in the formation of a 7-norbornenyl type radical could be made by such a study.

Synthesis of Aldehydes.—The synthesis of aldehydes **5** and **6** employed a Wittig reaction between ketone **7**

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[1] Paper V: J. W. Wilt and E. Vasiliauskas, *J. Org. Chem.*, **35**, 2410 (1970).

[2] Taken from a portion of the dissertation of E. V., Loyola University of Chicago, 1970. Some of this material was presented at the Third Great Lakes Regional Meeting of the American Chemical Society, DeKalb, Ill., June 5–6, 1969, Abstracts of Papers, p 58.

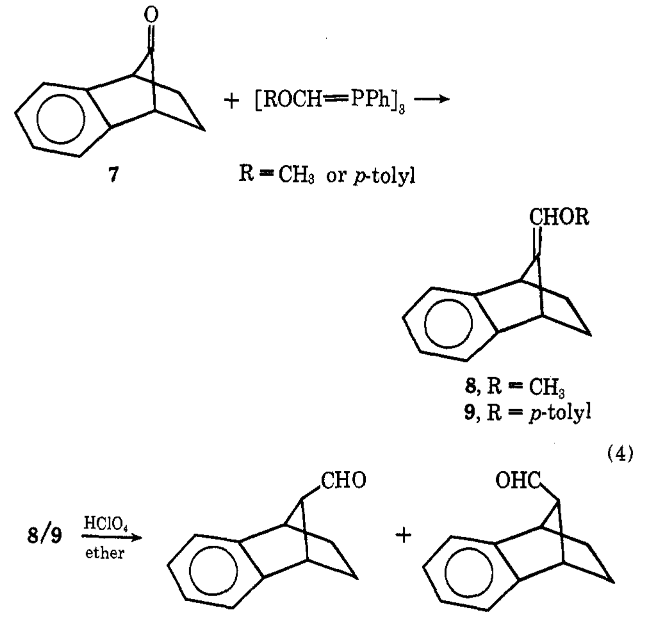
[3] NDEA Fellow, 1966–1969.

[4] *Cf.* H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968).

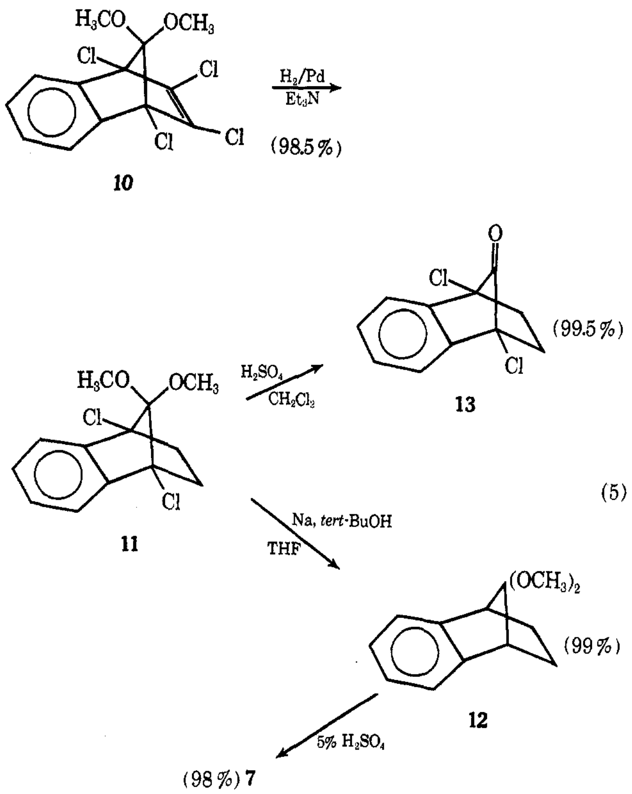
[5] J. W. Wilt and A. A. Levin, *J. Org. Chem.*, **27**, 2319 (1962).

[6] Some claims, strong and otherwise: J. W. Wilt, G. Gutman, W. J. Ranus, Jr., and A. R. Zigman, *ibid.*, **32**, 893 (1967); J. Warkentin and E. Sanford, *J. Amer. Chem. Soc.*, **90**, 1667 (1968); H. O. Ohorodnyk and D. P. Santry, *ibid.*, **91**, 4711 (1969). The counterclaims: S. J. Cristol and A. L. Noreen, *ibid.*, **91**, 3969 (1969); P. Bakuzis, J. K. Kochi, and P. J. Krusic, *ibid.*, **92**, 1434 (1970).

and the ylide from either methoxymethylene-[7] or *p*-tolyloxymethylene-[8] triphenylphosphorane, formed *in situ* from the appropriate phosphonium salt (eq 4).[9]



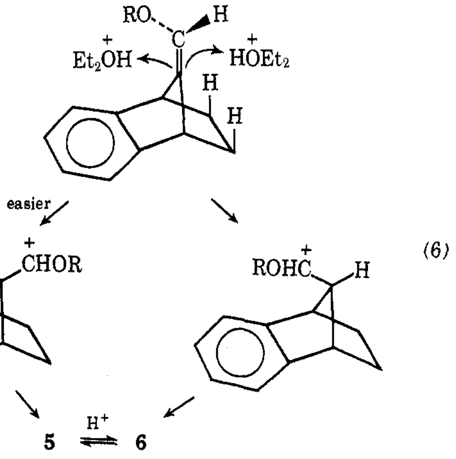
Benzonorbornen-7-one (**7**) is known,[10] but during this work a convenient new synthesis was developed.[11] The sequence (eq 5) commenced with **10**[1] and proceeded *via* two reduction processes[12] to **11**[13] and **12**, respectively. Ketals **11** and **12** readily afforded ketones **7** and **13** upon hydrolysis. Full details are given in the Experimental Section.



The Wittig reaction in eq 4 proceeded better with dimsyl sodium[14] as the ylide-generating base. For example, enol ether **8** (R = CH$_3$) was produced in 55% yield in this way as compared to 20% when *n*-butyllithium was used. Acidic hydrolysis of enol ether **8** or **9** was best achieved with ethereal perchloric acid.[7] Somewhat better yields in these two steps were achieved with R = CH$_3$ (55 and 84%) rather than with R = *p*-tolyl (49 and 61%).

The acidic hydrolysis of either enol ether **8** or **9** led to the same product, a mixture of aldehydes **5** (69.8%) and **6** (30.2%). Extensive efforts by gas–liquid partition chromatography failed to separate the epimers, although partial resolution was achieved. Careful distillation also changed the composition somewhat, but again the epimers were inseparable under any conditions tried.

The preferential formation of **5** rather than **6** upon hydrolysis of the enol ethers may reflect a kinetic favorability for protonation of the enolic double bond from the syn side (leading to anti aldehyde). Anti protonation would possibly be hindered by the exo ring H's (eq 6). Of course thermodynamic control of the product *via* epimerization through the enol of **5** and **6** is also conceivable. However, *nucleophilic* attack on ketone **7**[9a,15] and 7-norbornenone[16] favors syn approach kinetically, and later observations (*vide infra*) imply that the syn aldehyde **6** would be preferred over the anti epimer **5** if an equilibrium were established between them.[17] In any case no hydrolytic conditions



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[7] S. G. Levine, *J. Amer. Chem. Soc.*, **80**, 6150 (1958).

[8] G. Wittig, W. Böll, and K. Krück, *Chem. Ber.*, **95**, 2514 (1962).

[9] For other Wittig reactions of **7**, *cf.* (a) H. Tanida, Y. Hata, S. Ikegami, and N. Ishitobi, *J. Amer. Chem. Soc.*, **89**, 2928 (1967); (b) R. Muneyuki and H. Tanida, *ibid.*, **90**, 656 (1968).

[10] (a) P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960). (b) For a recent ozonation procedure to **7**, *cf.* R. Muneyuki and H. Tanida, *J. Org. Chem.*, **31**, 1988 (1966).

[11] Independently, a similar route was recently reported by P. F. Ranken and M. A. Battiste, *ibid.*, **36**, 1996 (1971). We thank Dr. Battiste for a preprint of their work. No detailed discussion of the sequence in 5 is given here because the sequence mirrors others which have been used and discussed for the nonbenzo analog.[12]

[12] *Cf.* (a) K. V. Sherer, *Tetrahedron Lett.*, 5685 (1966); (b) P. G. Gassman and P. G. Pape, *ibid.*, 9 (1963); *J. Org. Chem.*, **29**, 160 (1964).

[13] Some additional chemistry of ketal **11** and the ketone **13** obtained from it by hydrolysis will be reported in a subsequent paper of this series.

[14] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 866 (1962).

[15] K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, 9 (1966).

[16] J. Warkentin, *Can. J. Chem.*, **48**, 1391 (1970). Calculations indicate that the methano bridge in 7-norbornenone is bent back toward the saturated ethano arm, favoring syn attack on the carbonyl group. *Cf.* S. Yankelevitch and B. Fuchs, *Tetrahedron Lett.*, 4945 (1967).

[17] The situation is confused, however. Muneyuki and Tanida[9b] reported that catalytic hydrogenation of ethyl benzonorbornenylidene-7-acetate over platinum oxide (usually kinetic control) gave mainly (87%) reduction from the anti side whereas use of palladium on charcoal (usually thermodynamic control) gave predominantly (60%) syn reduced product. These are opposite to expectation and perhaps reflect the different type process (heterogeneous) involved.

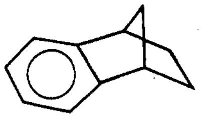
were found that favored **6** over **5** from either enol ether.

Structural Assignments.—The assignment of structure to these aldehydes rests on the nmr position of the aldehydic proton doublet in each case. In **6**, this proton is positioned in the deshielding zone above the plane of the aromatic ring[18] and the doublet resonance was at δ 9.22. In **5**, contrariwise, the aldehydic doublet resonance was at δ 9.57. Integration of these signals then allowed a ready determination of the composition of any mixture isolated by preparative glpc or distillation. An interesting additional difference between **5** and **6** was the spin–spin coupling constant (J value) for the doublet, 0.5 Hz for **5** *vs.* 3.5 Hz for **6**. Neither value changed (<0.3 Hz) upon variable-temperature nmr studies over the range 25–150°; so the J value difference presumably is not due to conformational preferences in the aldehydes. Possibly other molecular features, such as the bridge angle at C-7 and/or the effective electronegativity of the carbonyl group, differ in the epimers and cause the disparate J values.[19] Further study, including low-temperature nmr studies, are in progress on this point.

The resonance position of the 7 proton in **5** and **6** deserves comment. In a number of 7-substituted benzobornenes, the syn 7 proton is shielded by the aromatic ring and its resonance position is upfield relative to that for the anti 7 proton in the epimer.[20] The reverse is true for norbornene and benzonorbornene themselves[15,21] and for the aldehydes **5** and **6**. The assignment in the latter compounds seems secure nonetheless because the syn 7 proton in **5** is a multiplet (δ 2.55) evidencing coupling with the bridgehead and endo ring protons as well as the aldehydic proton. In **6**, the anti 7 proton is a doublet tripleted (δ 2.42) as would be expected for larger coupling to the aldehydic proton (J = 3.5 Hz) and weaker coupling ($J \sim$ 1.5 Hz) to the bridgehead protons. It has been claimed[22] that the *lower* field resonance for syn 7 protons in norbornene is general, with a reversal expected when anisotropic functions complicate matters. Presumably the aldehyde function in **5** and **6** is not such a complicating function. The entire rationale for bridge proton resonance positions in 7-substituted norbornenes obviously needs development.

Decarbonylation and Related Studies on Aldehydes 5 and 6.—Liquid-phase decarbonylation of a neat aldehyde mixture (**5**:**6** = 69.8:30.2) in the customary fashion[23] using 10–30 mol % di-*tert*-butyl peroxide at 180° for 3 hr yielded benzonorbornene (**14**, 60.6%), carbon monoxide (85%), ill-defined higher molecular weight material (~20%), and recoverable initial aldehydes (~15%), as shown in eq 7.

The unusual feature of the process was that the recovered aldehyde mixture was now richer in the syn epimer

$5 + 6 \xrightarrow[\text{heat}]{\text{DTBP}}$  + CO + unknowns (7)

14

(**5**:**6** = 37.7:62.3), *indicating preferential loss of the anti aldehyde* **5**![24] This was confirmed by the results in Table I obtained from a different initial aldehyde mixture.

TABLE I

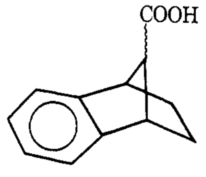
RATIO OF ALDEHYDES 5 AND 6 RECOVERED AFTER PARTIAL DECARBONYLATION

Reaction time, min[a]	5:6 Ratios[b]
0	73.6:26.4
95	60.4:39.6
141	54.0:46.0

[a] At 180°. [b] Determined by nmr analysis of the recovered aldehydic mixture isolated *via* glpc at the indicated time.

A similar reaction without peroxide gave only a 1.3% yield of **14**; so a radical chain process seems implicated in the formation of the products in eq 7.

In contrast to the peroxide-induced process, decarbonylation of aldehydes **5** and **6** with palladium on charcoal[25] at 194° led cleanly to **14** (97.5%). Only small amounts of unchanged aldehydes and their corresponding acids **15** were otherwise detected (eq 8). This result reemphasizes the utility of this method as a *preparative* decarbonylation technique (considerably superior to the peroxide method).

$5 + 6 \xrightarrow[\text{heat}]{\text{Pd/charcoal}} 14 +$  + CO (8)

15 (traces)

The faster decarbonylation observed under peroxidic conditions with the anti aldehyde **5** could be the result of π participation as in (eq 3). On the other hand, its faster decarbonylation could be due to easier chain transfer with **5** than with **6** (eq 9).

To evaluate these possibilities, the aldehyde mixture was treated with benzoyl peroxide and carbon tetrachloride under reflux at ~77° or with di-*tert*-butyl peroxide (DTBP) and benzotrichloride at 180°.[26] The resulting mixture was then treated with methanol and the products were isolated by gas chromatography (eq 10). The data from this study are given in Table II.

The assignment of structure to the esters **16** and **17** was again by nmr evidence. The syn epimer **17** exhibited the methyl singlet resonance at δ 3.38, upfield as expected[18] from the methyl resonance of **16** at δ 3.63. Integration of these singlets then allowed a determination of the ester ratio.

The formation of esters **16** and **17** with no apparent **14** indicates that the acyl radicals from the aldehydes were effectively trapped by the chlorine donors used as

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[18] L. M. Jackson, "Applications of Nuclear Magnetic Resonance in Organic Chemistry," Macmillan, New York, N. Y., 1959, p 125. See also D. J. Pasto and C. R. Johnson, "Organic Structure Determination," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 172.

[19] M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

[20] J. W. Wilt and P. J. Chenier, *J. Org. Chem.*, **35**, 1562 (1970), and references cited therein.

[21] B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Snyder, *J. Amer. Chem. Soc.*, **90**, 3721 (1968).

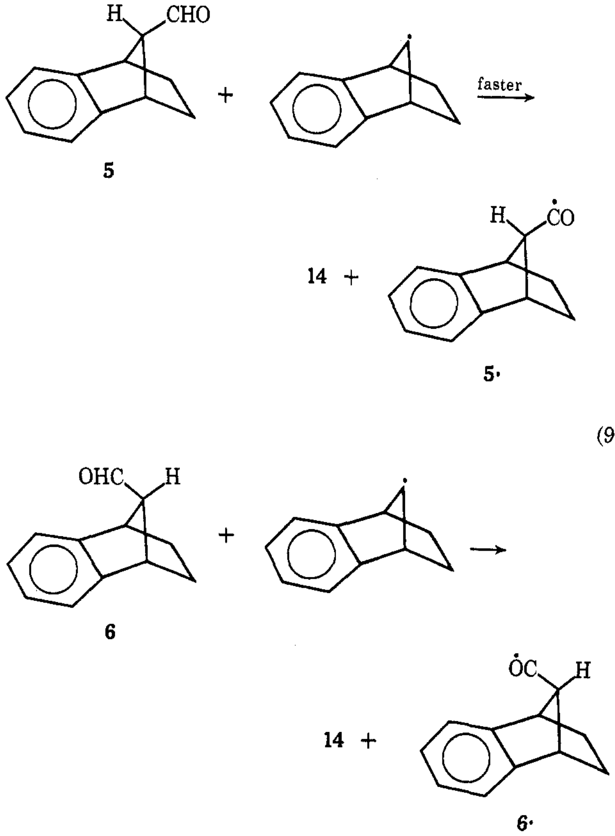
[22] A. P. Marchand and J. E. Rose, *ibid.*, **90**, 3724 (1968). These authors also note that the *coupling* of bridge protons in norbornenes is better evidence for their stereochemistry than is their *chemical shift*.

[23] *Cf.* J. W. Wilt, L. L. Maravetz, and J. F. Zawadzki, *J. Org. Chem.*, **31**, 3018 (1966), and references to earlier studies cited therein.

[24] The **5**:**6** ratio is of course time dependent (see Table I). However, in this typical example **5** was some fourfold faster in the process than **6**.

[25] J. W. Wilt and V. P. Abegg, *J. Org. Chem.*, **33**, 923 (1968).

[26] This technique was used some time ago by S. Winstein and F. H. Seubold, Jr., *J. Amer. Chem. Soc.*, **69**, 2916 (1947), and more recently by D. E. Applequist and L. Kaplan, *ibid.*, **87**, 2194 (1965).



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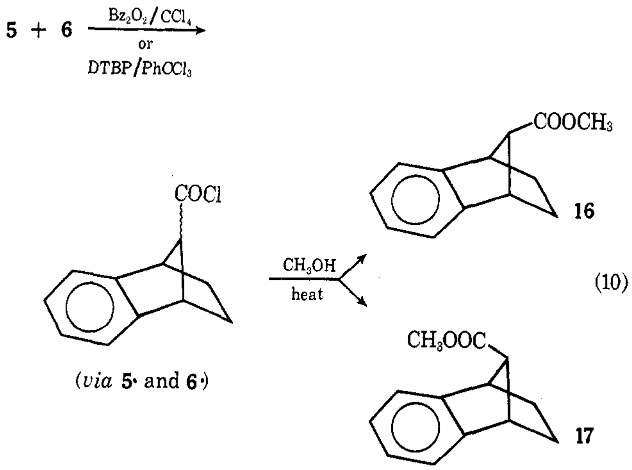

(10)

TABLE II

TRAPPING STUDIES ON ACYL RADICALS 5· AND 6·

5:6	Yield of esters 16 + 17, %	16:17
77.2:22.8[a]	93.5	76.0:24.0[c]
65.1:34.9[b]	68.9	65.3:34.7[c]

[a] Initial ratio of aldehydes 0.3 *M* in CCl_4 heated under reflux for 0.5 hr. Benzoyl peroxide was used as the initiator. [b] Initial ratio of aldehydes 0.68 *M* in benzotrichloride held at 180° for 4 hr. DTBP was used as the initiator. [c] By nmr analysis of material isolated *via* glpc.

solvents. The virtual identity of the initial aldehydes and final ester anti:syn ratios at two widely different temperatures and with two solvents of somewhat different chain-transfer ability[27] strongly indicates that π participation analogous to eq 3 was *not* a detectable cause of the faster decarbonylation of **5**.[28] Rather, better chain transfer with the anti aldehyde probably occasioned the different decarbonylation rates as shown earlier in Table I. Such a difference in chain-transfer ability between aldehydes has been suggested before[29] and in the present case may be related to the different steric environment of the aldehydic hydrogens in **5** *vis-à-vis* **6**. Available data does not allow, however, a definitive conclusion in this regard.

Attempts to epimerize the ester mixture **16** + **17** were only partly successful. Heating a mixture of esters with sodium methoxide in methanol for various times led to enrichment of the syn epimer **17**. However, recovery of the ester mixture was not quantitative after each heating period and the anti:syn ratio did not level off; so the meaning of the syn enrichment is not immediately clear. If the enrichment is due to a thermodynamic preference for the syn epimer, it lends credence to the aforementioned kinetic preference for the anti aldehyde formed upon hydrolysis of the enol ethers.

In summary, the peroxide-induced decarbonylation of the epimeric benzonorbornene-7-carboxaldehydes proceeded faster with the anti compound. Evidence from chain-transfer experiments indicated that this favorability was not due to any pronounced preferential decarbonylation of the acyl radical derived from the anti aldehyde. More probably the favorability may be ascribed to differences in the chain-transfer abilities of the epimeric aldehydes. No evidence supporting our earlier suggestion of possible π electron assistance in such systems was found.

Experimental Section

Melting points were taken on a calibrated Fisher-Johns block. Boiling points are uncorrected. Infrared spectra (λ) were determined on a Beckman IR-5A instrument. Only prominent or structurally significant absorptions are listed (in microns). Nuclear magnetic resonance spectra were taken on a Varian A-60A spectrometer. Values are given in parts per million (δ) downfield from internal TMS. The usual splitting abbreviations are used. Integrations of signals agreed with the structural assignments. Gas-liquid partition chromatography (glpc) was done on a Varian Aerograph A-90P chromatograph with helium gas as carrier. Peaks were disc-integrated. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

1,4-Dichloro-7,7-dimethoxybenzonorbornene (11).—1,2,3,4-Tetrachloro-7,7-dimethoxybenzonorbornadiene (**10**,[1] 5.0 g, 14.7 mmol) was hydrogenated at 25° over palladium on carbon (5%, 1.0 g) in 95% ethanol (200 ml) containing excess triethylamine (70 ml).[12a] After 1.5 hr the filtered solution was evaporated to dryness. Water and ether (150 ml of each) were added and the mixture was shaken. The ether phase was separated and combined with ether washes of the aqueous phase. After a wash with potassium carbonate solution (10%), the combined ether solution was dried ($MgSO_4$) and evaporated. The residual oil was distilled to afford colorless **11**: yield 3.95 g (98.5%); bp 117–118° (0.55 mm); $n^{27}\text{D}$ 1.5488; $d^{29}{}_4$ 1.2843; λ (neat) 6.84, 8.90–9.03 μ (OCH_3); nmr (CCl_4) δ 7.46 (s, ArH), 3.74 (s, anti OCH_3), 3.40 (s, syn OCH_3), 2.55 (dd, exo ring H's, $J_{\text{exo,endo}}$ = 11 Hz, J_{vic} = 4.5 Hz), 1.58 (dd, endo ring H's). The analytical sample was collected by glpc at 170° using a column of 20% Reoplex 400 on 30/60 mesh Gas-Chrom (column R).

Anal. Calcd for $C_{13}H_{14}O_2Cl_2$: C, 57.16; H, 5.16. Found: C, 57.41; H, 5.22.

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[27] R. A. Gregg and F. R. Mayo, *J. Amer. Chem. Soc.*, **75**, 3530 (1953), report the following chain transfer constants at 60° in styrene polymerization: CCl_4, 0.920 × 10^{-2}; $C_6H_5CCl_3$, 0.575 × 10^{-2}.

[28] It remains a possibility, nonetheless. The acyl radicals may simply undergo chain transfer with the chlorine donor solvent faster than they lose carbon monoxide, even though this latter process may *still* be *potentially* faster in the anti epimer **5**. If so, however, we feel that the difference between **5** and **6** in this regard cannot be very large or significant.

[29] J. W. Wilt and H. Philip, *J. Org. Chem.*, **25**, 891 (1960).

7,7-Dimethoxybenzonorbornene (12).—To a vigorously stirred solution of ketal **11** (10.0 g, 36.7 mmol) in dry *tert*-butyl alcohol (50 ml) and tetrahydrofuran (210 ml) under nitrogen was added finely chopped sodium metal (27 g, 1.17 g-atoms).[12b] The mixture was refluxed for 18 hr. Methanol was next slowly added to destroy the excess sodium. The solution was poured into cold water (1.5 l.) and extracted with ether (3 × 500 ml). The ether extracts were combined, washed with water, and dried ($MgSO_4$). Removal of solvent left quite pure **12** as an oil that slowly solidified. Distillation in a short-path apparatus, bp *ca.* 90° (0.05 mm), gave colorless product: yield 7.40 g (99%); mp 49–50°; λ (neat) 6.83, 8.84, 9.08–9.38 μ (OCH_3); nmr (CCl_4) δ 7.11 (s, ArH), 3.25 (s, anti OCH_3), 3.21 (m, bridgehead H's), 3.02 (s, syn OCH_3), 2.07 (m, exo ring H's), 1.07 (m, endo ring H's). The analytical sample was collected by glpc at 175° using column R.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.60; H, 7.94.

1,4-Dichlorobenzonorbornen-7-one (13).—A mixture of ketal **11** (4.97 g, 18 mmol), methylene chloride (100 ml), and concentrated sulfuric acid (40 ml) was stirred at 25° for 24 hr. The methylene chloride phase was separated and combined with methylene chloride washes of the sulfuric acid phase. The combined organic material was washed to neutrality, dried ($MgSO_4$), and evaporated. The yellow oily residue was dissolved in pentane and precipitated by chilling to −50°. Ketone **13** formed white needles upon recrystallization from pentane: yield 3.97 g (99.5%); mp 69–69.5°; λ (KBr) 5.51 μ (CO); nmr (CCl_4) δ 7.79 (s, ArH), 2.85–1.85 (sym m, ring H's).

Anal. Calcd for $C_{11}H_8OCl_2$: C, 58.18; H, 3.55. Found: C, 57.88; H, 3.44.

The yellow **2,4-dinitrophenylhydrazone** derivative was best prepared with the phosphoric acid–ethanol solution of the reagent,[30] mp 220.5–221.5° dec.

Anal. Calcd for $C_{17}H_{12}O_4N_4Cl_2$: N, 13.76. Found: N, 13.82.

Benzonorbornen-7-one (7).—The ketone was prepared as reported by Oppenauer oxidation of *anti*-7-benzonorbornenol.[10a] Small-scale preparation was also effected by oxidation of this alcohol with chromium trioxide in pyridine. A convenient alternative method involved hydrolysis of ketal **12** (5 g, 24.5 mmol) with dilute sulfuric acid (5%, 250 ml) for 20 hr at 50°. The ketone was isolated by extraction with ether (2 × 125 ml). The water-washed extract was dried ($MgSO_4$) and distilled to afford pale yellow **7** (3.90 g, 98%, spectra agreed with those reported[10a,11]).

7-Methoxymethylenebenzonorbornene (8).—Dimsyl sodium (33 mmol) was prepared in dry dimethyl sulfoxide (15 ml) as reported.[31] To this at 20° under nitrogen was added methoxymethyltriphenylphosphonium chloride[32] (11.25 g, 33 mmol, mp 199–202° dec) dissolved in warm dimethyl sulfoxide (45 ml). The dark red solution of the phosphorane was stirred at 25° for 10 min and then ketone **7** (5.20 g, 33 mmol) was added slowly with external cooling to maintain the temperature at 30–35°. The reaction mixture was stirred at 35° for 30 min and at 55° for 16 hr. The cooled solution was added to water (150 ml) and extracted with pentane (3 × 200 ml). The combined pentane extracts were washed well with water and brine, dried ($MgSO_4$), and evaporated. The residual oil was chromatographed through alumina (100 g) and then distilled to yield **8** as a colorless oil: yield 3.35 g (54.8%); bp 81–85° (0.08 mm); λ (neat) 5.81, 8.21, 8.56–8.72, 8.97 μ ($C{=}COCH_3$); nmr (CCl_4) δ 7.22 (m, ArH), 5.67 (s, vinyl H), 4.09 (m) and 3.52 (m, bridgehead H's), 3.49 (s, OCH_3), 1.95 (m, exo ring H's), 1.25 (m, endo ring H's). The analytical sample was collected by glpc at 178° using column R.

Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.64; H, 7.53.

A similar reaction (24-mmol scale) of **7** and the phosphorane using *n*-butyllithium (46 mmol) in ether as base gave only a 20.3% yield of **8**.

7-*p*-Tolyloxymethylenebenzonorbornene (9).—Dimsyl sodium (21 mmol) in dry dimethyl sulfoxide (60 ml) was used to convert *p*-tolyloxymethyltriphenylphosphonium chloride[8] (8.8 g, 21 mmol, mp 195–198°) to the phosphorane as described above for **8**. Reaction with ketone **7** (3.39 g, 21 mmol) again as described above, led to enol ether **9**, best isolated by glpc (20% SE-30 on 30/60 mesh Gas-Chrom column at 233°) as a pale yellow oil: yield 2.77 g (49.4%); $n^{29}D$ 1.5985; λ (neat) 5.81, 8.00, 8.18, 8.99 μ ($C{=}COR$); nmr (CCl_4) δ 6.77–7.34 (m, ArH), 6.12 (s, vinyl H), 4.15 (m) and 3.64 (m, bridghead H's), 2.29 (s, $ArCH_3$), 2.04 (m, exo ring H's), 1.32 (m, endo ring H's).

Anal. Calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92. Found: C, 87.50; H, 6.75.

***anti*- (5) and *syn*-Benzonorbornene-7-carboxaldehyde (6).**—Perchloric acid (17 ml of 70% reagent grade material) was added dropwise to ether (70 ml) with good stirring. Enol ether **8** (4.10 g, 22 mmol) was added and the solution was heated under reflux for 2 hr. Water (100 ml) and ether (100 ml) were then added to the cooled solution. The material was vigorously shaken and the ether layer was separated. The aqueous phase was extracted with several more portions of ether. The ether layer and combined extracts were washed several more times alternately with water and sodium bicarbonate solution and then dried ($MgSO_4$). Distillation produced aldehydes **5** and **6** as a colorless oil: yield 3.23 g (84.4%); bp 88–93° (0.8 mm); λ (neat) 3.60, 3.72, 5.85 μ (-CHO); nmr (CCl_4) δ 9.57 (d, -CHO of **5**, $J \cong 0.5$ Hz), 9.22 (d, -CHO of **6**, $J = 3.5$ Hz), 7.07 (m, ArH), 3.55 (m, bridgehead H's), 2.55 (m, 7-H of **5**), 2.42 (partially obscured doublet of triplets, 7-H of **6**), 1.95 (m, exo ring H's), 1.18 (endo ring H's).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.69; H, 7.02. Found: C, 83.70; H, 7.09.

The J values for the aldehydic protons were unchanged over the temperature range 25–148°. The doublet of triplets for the 7-H of **6** has J values of 3.5 and *ca.* 1.5 Hz.

The **2,4-dinitrophenylhydrazone** upon precipitation had mp 180–190° dec. Repeated recrystallization from ethanol–ethyl acetate apparently fractionated the mixture to give an analytical sample, mp 206–209° dec, although which epimeric derivative was obtained is unknown.

Anal. Calcd for $C_{18}H_{16}O_4N_4$: N, 15.90. Found: N, 15.82.

Analogous hydrolysis treatment of enol ether **9** gave a 67.3% yield of **5** and **6**. Analysis of the aldehyde mixture from either enol ether by integration of the nmr signal at δ 9.57 and 9.22 gave a ratio **5**:**6** of 2.3:1. Separation of the mixture at 180–200° was unsuccessful on the following glpc columns: Reoplex 400, Flexol 8N8, SE-30, neopentyl glycol succinate, Carbowax 20M, and Apiezon L. Partial resolution was achieved at 185° with an Apiezon N column.

The aldehydes were substantially oxidized to acids at 25° upon exposure to air as a thin film for 3 days. The unoxidized aldehydes were decanted from the crystalline acid(s). From an initial mixture of **5**:**6** of 68.3:31.7 the recovered aldehydes were almost unchanged in proportion by nmr analysis (**5**:**6**, 69.3:30.7). The crystalline material was taken up in dilute sodium hydroxide (10%), washed with ether, and then precipitated by the addition of dilute hydrochloric acid. The crude product, mp 147–151°, was recrystallized several times from hexane to give white crystals of **benzonorbornene-*anti*-7-carboxylic acid**: mp 153–154°; λ (Nujol mull) 5.92 μ (COOH); nmr (CCl_4) δ 10.58 (s, COOH), 7.14 (s, ArH), 3.65 (m, bridgehead H's), 2.85 (close pentuplet, (7-H), 2.17 (m, exo ring H's), 1.25 (m, endo ring H's).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.74; H, 6.58.

The anti nature of the acid is a provisional assignment based upon the pentuplet nature of the syn 7 proton. This is the expected splitting for this proton because of probable coupling with the bridgehead and endo ring protons. Presumably the syn acid was fractionated away upon the recrystallizations.

Peroxide-Induced Decarbonylation of Aldehydes 5 and 6.—A known mixture of aldehydes was mixed with freshly distilled di-*tert*-butyl peroxide (10 mol %) and heated in a gas-collecting system under helium. Two additional increments of peroxide (10 mol % each) were added to the mixture by syringe through a septum cap at ~1-hr intervals when gas evolution slackened. Several reactions were conducted at 180 ± 1° and for 3–4 hr. The collected gas was analyzed for carbon monoxide *via* glpc on a molecular sieves 13X column at 25°, using calibration data from injected authentic carbon monoxide. The brown oil remaining after reaction was also analyzed *via* glpc. Benzonorbornene (**14**) and unreacted aldehydes **5** and **6** were the only volatile products. Distillation of the reaction material again gave only these products along with a resinous residue. A typical reaction on 0.3858 g (2.2 mmol) of aldehydes (**5**:**6**, 69.8:30.2) gave carbon

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[30] L. F. Fieser, "Organic Experiments," 2nd ed, Raytheon Education Co., Lexington, Mass., 1968, p 98.

[31] R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 1128 (1963).

[32] G. Wittig and M. Schlosser, *Chem. Ber.*, **94**, 1373 (1961).

monoxide (42.7 ml at STP, 85%), benzonorbornene (**14**, 0.1958 g, 1.4 mmol, 60.6%), unreacted aldehydes (~15%, **5**:**6**, 37.7:62.3), and uncharacterized distillation residue (~20%).

Other reactions were sampled by syringe through the septum at various intervals and the aldehyde composition was ascertained by nmr analysis (see Table I).

A reaction carried out as above but without the di-*tert*-butyl peroxide afforded **14** in small amount (1.3%). The aldehydic mixture was essentially unchanged otherwise.

Palladium-Promoted Decarbonylation of Aldehydes 5 and 6.—Aldehydes **5** and **6** (0.4935 g, 2.9 mmol) and palladium on charcoal (5%, 0.495 g) were heated at 194 ± 1° for 3.5 hr, at which time the evolution of carbon monoxide effectively ceased. Analysis of an aliquot of the residual oil by glpc indicated the presence of **14** (97.5%) and unreacted aldehydes. Microdistillation of the remainder afforded **14**, with a distillation residue comprised mainly of acids **15**. Benzonorbornene was *isolated* by distillation in 91.5% yield.

Reaction of Aldehydes with Carbon Tetrachloride and Benzotrichloride.—An aldehydic mixture (**5**:**6**, 77.2:22.8, 0.5226 g, 3.0 mmol), together with recrystallized benzoyl peroxide (0.07 g, 0.3 mmol) and purified carbon tetrachloride (10 ml), were heated at reflux under nitrogen. After 30 min another 0.07 g of peroxide was added and heating was continued for another 30 min. Dry methanol (6 ml) was then added to the cooled solution and the material was again heated at reflux for 20 min. Water was added to the cooled solution and the carbon tetrachloride phase was separated. The material was washed with sodium bicarbonate solution (saturated, 10 ml) and water until it was neutral. The dried solution ($MgSO_4$) was distilled free of solvent and chloroform [δ 7.42 (s)] formed in the reaction. The oil remaining was separated by glpc on column R at 190° into methyl benzoate (from the peroxide) and **methyl benzonorbornene-*anti*- and -*syn*-7-carboxylates** (**16** and **17**, respectively, 0.57 g, 93.5%). The ratio of **16**:**17** was 76.0:24.0 by nmr analysis. The esters were obtained as a colorless oil: λ (neat) 5.78 μ (C=O); nmr (CCl_4) δ 7.09 (s, ArH), 3.64 (s, OCH_3 of anti ester **16**), 3.56 (m, bridgehead H's), 3.38 (s, OCH_3 of syn ester **17**), 2.68 (m, 7-H), 2.05 (m, exo ring H's), 0.95 (m, endo ring H's).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.07; H, 7.13.

The esters were separable on a 0.25 in. × 6 ft Apiezon N column (20% on 30/60 mesh Gas-Chrom) at 180°.

Reaction of the aldehydes (**5**:**6**, 65.1:1.34.9, 0.5841 g, 3.4 mmol), di-*tert*-butyl peroxide (0.05 g, 0.3 mmol), and freshly distilled benzotrichloride (5 ml) was carried out under helium at 180 ± 1° for 4 hr. Additional peroxide (0.05-g increments) was added at 75-, 83-, 64-, and 65-min intervals. The reaction was treated with methanol and processed as described above. The products observed were some **tolane tetrachloride** (from the solvent, mp and lit.[33] mp 160–161°), esters **16** and **17** (68.9%, **16**:**17**, 65.3:34.7) and unidentified products (~25%) possessing carbonyl and monosubstituted aromatic functions (λ 5.75–5.78, 13.4, and 14.4 μ).

Attempted Epimerization of Esters 16 and 17.—Sodium methoxide (4.0 mmol) was freshly prepared in methanol (3 ml). Esters **16** and **17** (80:20, 0.83 g, 4 mmol) were added in methanol (2 ml) and the solution was heated under reflux for various times. The cooled solution was diluted with water and quickly extracted with ether. The ether extracts were washed, dried ($MgSO_4$), and evaporated. The remaining oil was then analyzed by nmr to obtain the ratio of esters (OCH_3 resonances). After each determination the esters were heated for an additional period and processed again. The data are given in Table III.

TABLE III

EPIMERIZATION OF ESTERS 16 AND 17

Reaction time,[a] hr	16:17 Ratio	Recovery, %
0	80:20	
0.5	79:21	91.7
3.5	71.5:28.5	88.2
9.5	67.3:32.7	79.2
26.8	55.4:44.6	79.4
89.0	33.4:66.6	62.0
210[b]	22.2:77.8	65.4

[a] Under reflux in methanol. [b] Too little material available after this time for further study.

Registry No.—**5**, 34225-91-7; **6**, 34225-92-8; **6** DNP, 34201-91-7; **8**, 34201-92-8; **9**, 34201-93-9; **11**, 34201-94-0; **12**, 29370-70-5; **13**, 34201-96-2; **13** DNP, 34201-97-3; **16**, 34225-93-9; **17**, 34225-94-0; benzonorbornene-*anti*-7-carboxylic acid, 34225-95-1.

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[33] D. C. Sayles and M. S. Kharasch, *J. Org. Chem.*, **26**, 4210 (1961).