thermolysis products. Individual samples of Ix, In, and a 47.9: 52.1 mixture of *cis*-III and *trans*-III were heated at 198.9° for 16 hr. Samples of Ix and In also were heated at 220° for 5.5 hr. A sample of the 47.9:52.1 mixture of *cis*-III and *trans*-III was heated at 135° for 100 hr as a check on product isomerization under thermolysis product conditions.

Direct Photolysis Products. The following illustrates the general procedure used to determine the product composition from direct irradiation of Ix and In in solution. A 5-ml sample of a 0.01 *M* solution of azo compound in pentane in a 10-ml Pyrex tube was degassed by three freeze–pump–thaw cycles and sealed under *ca.* 0.6 mm nitrogen. The sample tube was taped to a water-cooled quartz immersion well and irradiated for 24 hr with a 200-W Hanovia Type S lamp. Following irradiation the sample was analyzed directly by vpc. A pentane solution 0.3 *M* in piperylene was used for the quenching experiments.

Solid-phase direct photolysis was accomplished with samples of azo compound which had been degassed and sealed under nitrogen in Pyrex tubes. A sample tube was strapped to a transparent Pyrex vacuum dewar flask which then was immersed in a Dry Ice–methanol bath at −80°. After crystallization appeared to be complete[32] the sample was irradiated for 15 hr with the 200-W lamp. The lamp was placed directly in the dewar flask and was cooled with a stream of air.

Sensitized Photolysis Products. The following is typical of the procedure used for the sensitized photodecomposition studies of Ix and In. Samples (5 ml) of cyclohexane solutions 0.01 *M* in azo compound and 0.05 *M* in benzophenone were placed in 20-ml quartz test tubes having 14/20 standard taper joints on the top. The tubes fitted with a stopcock were degassed by three or more freeze–pump–thaw cycles and closed under *ca.* 0.6 mm nitrogen. Irradiation was performed on a "merry-go-round" assembly in a Rayonet–Griffin–Srinivasan photochemical reactor using a 2537-Å light source. Experiments with and without piperylene were carried out simultaneously under identical conditions. Following irradiation, analyses were performed by vpc on product solutions which had been flash distilled (kettle temperature *ca.* 60°) under low vacuum into a Dry Ice–acetone-cooled trap.

For sensitized decompositions conversion to product was complete in <20 min. This was estimated by vpc by measuring the development of product against 1,2-dimethoxyethane as an internal standard. The ratio of products formed in the presence of sensitizer did not change during irradiation times from 5 to 75 min.[35]

Thermal Rearrangements of Some 1,3-Methanoindans (Benzobicyclo[2.1.1]hexenes)[1]

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Abstract: 1,3-Methanoindan (1) thermally isomerizes to 1,1a,6,6a-tetrahydrocycloprop[*a*]indene (2) in a quantitative yield. In the case of the *anti*-2-chloro derivative (3), the reaction proceeds with a quantitative formation of naphthalene. When the reaction was carried out with methyl *anti*-2-chloro-1,3-methanoindan-*exo*-8-carboxylate (5) (or its *endo* isomer (8)), the products were a 20% yield of methyl α-naphthalenecarboxylate (6) and a 55% yield of methyl β-naphthalenecarboxylate (7) (or 5% 6 and 80% 7). The rates and activation parameters of the reactions were determined. Relative to the parent 1, the monosubstituted 3 and methyl 1,3-methanoindan-*endo*-2-carboxylate (19) react at rates enhanced by factors of 40–50. However, the rate of the disubstituted 5 was approximately only twice as much as those of 3 and 19 and that of 8 was not significantly different from those of 3 and 19. The results are discussed in radical mechanisms as well as a [1,3]-sigmatropic rearrangement.

Derivatives of 1,3-methanoindan, the smallest bridged benzocyclene known, were first synthesized by us[2] and Pomerantz,[3] independently. The solvolytic behavior of the derivatives and evidence for large participation of the benzene ring were recently reported.[4] As a continuation of our research on this ring system, this paper deals with the behavior in thermolysis.

Results

The syntheses of all but one reactants employed were reported by us.[2,4] The exception was prepared according to substantially the same methods as above (Experimental Section). Heating a carbon tetrachloride solution of 1,3-methanoindan (1) at 200° for 15 hr

(9 half-lives) in a tube sealed under nitrogen atmosphere gave a single product as analyzed by vpc. The product was isolated and its structure established to be 1,1a,6,6a-tetrahydrocycloprop[*a*]indene (2) by comparison with an authentic sample.[5] The yield estimated by vpc was roughly quantitative. When the reaction was carried out with *anti*-2-chloro-1,3-methanoindan (3), a quantitative formation of naphthalene (4) was observed. It is therefore reasonable to consider that a chloro derivative(s) of 2 or an intermediate(s) leading to it (them) converts into 4 with elimination of hydrogen chloride under the reaction conditions.

Of special interest is that the reaction with methyl *anti*-2-chloro-1,3-methanoindan-*exo*-8-carboxylate (5) (160°, 5 hr which corresponds to 6 half-lives) produced methyl α-naphthalenecarboxylate (6) in 20% yield and its β isomer (7) in 55% yield and the reaction with the

(1) The numbering used in this paper is shown in the charts.
(2) H. Tanida and Y. Hata, *J. Amer. Chem. Soc.*, **88**, 4289 (1966).
(3) M. Pomerantz, *ibid.*, **88**, 5349 (1966).
(4) Y. Hata and H. Tanida, *ibid.*, **91**, 1170 (1969).

(5) A. L. Goodman and R. H. Eastman, *ibid.*, **86**, 908 (1964).

Table I. Rates in Thermolysis of 1,3-Methanoindans[a]
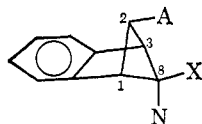
| Substituent | | | Temp, °C | k_1, sec⁻¹ | Calcd at 150° | | |
A	X	N			$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, cal/deg mol	Rel rate
H	H	H	150.0	8.12×10^{-7} [b]	38.4	3.5	1
			180.2	1.81×10^{-5}			
			199.4	1.06×10^{-4}			
Cl	H	H	150.0	3.33×10^{-5}	35.1	3.2	41
			170.0	2.29×10^{-4}			
Cl	COOMe	H	129.7	7.68×10^{-6}	37.7	10.9	86
			150.0	7.01×10^{-5}			
			160.0	2.29×10^{-4}			
Cl	H	COOMe	129.7	2.91×10^{-6}	36.0	4.8	30
			150.0	2.41×10^{-5}			
			170.0	1.92×10^{-4}			
H	H	COOMe	130.0	4.70×10^{-6}	35.4	4.3	49
			150.0	3.94×10^{-5}			
			170.0	2.90×10^{-4}			
Br	COOMe	H	150.0	6.24×10^{-5}			77

[a] Carried out with 0.05 mol solution in carbon tetrachloride. [b] Calculated by Arrhenius plots.

corresponding *endo*-8-carboxylate (8) (150°, 3 days which corresponds to 9 half-lives) produced 6 in 5% and 7 in 80% yield. These naphthalene derivatives were observed to be stable under the conditions and do not equilibrate. Thus it is demonstrated that the *endo*- and *exo*-carbomethoxyl groups originally located at the β position to the benzene ring, in part, rearranged to the α position.
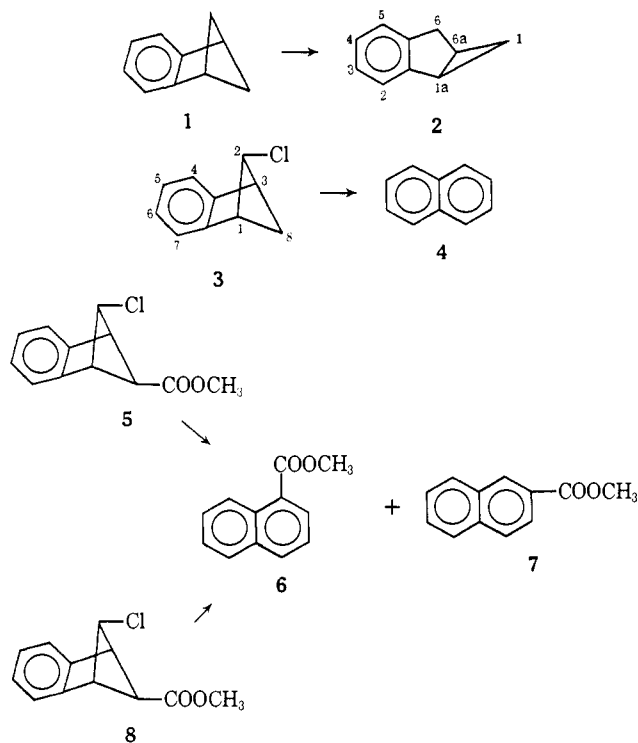

The reaction rates, measured by vpc or infrared spectra, and activation parameters are summarized in Table I. The rate of *anti*-2-bromo-1,3-methanoindan-*exo*-8-carboxylate was also measured to investigate the effect of leaving groups. The data show that the rates are accelerated by factors of 40–50 with an introduction

of the chloro or the carbomethoxyl group. Disubstitution by the chloro and carbomethoxyl groups at the same *exo* side as in 5 raises the rate by a factor of 86. However, compared to the monosubstitution, the effect of the second substituent is very small and shown as a factor of about 2 (86/41). When, as in 8, the first substitution is carried out from the *exo* side and the second substitution from the *endo* side, the effect of the second group is shown to be absent. No significant difference in rate was observed between 5 and *anti*-2-bromo-1,3-methanoindan-*exo*-8-carboxylate.

The use of other solvents such as pyridine and dioxane or no employment of solvents does not significantly affect the rate (Table II shows the data for 5) and product composition.

Discussion

Pyrolysis of norbornadiene leads to mixtures of cycloheptatriene and toluene.[6] Benzonorbornadiene, when heated at 370–380° (under static conditions[7c]),
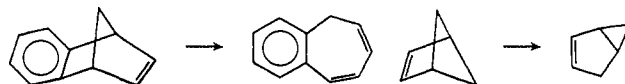
was reported to give 1,2-benzocycloheptatriene.[7] At higher temperatures, 1,2-benzocycloheptatriene is isomerized to 1- and 2-methylnaphthalenes.[7b] It has been suggested that the reactions initially form diradical intermediates by cleavage of the methano bridges.[6a,d,7b,c] The possibility of a concerted process in the reaction of benzonorbornadiene was also pointed out.[7c] The isomerization of bicyclo[2.1.1]hex-2-ene to bicyclo[3.1.0] hex-2-ene is very facile and was observed at 150–200°.[8] The thermolysis of 1 was observed at nearly the
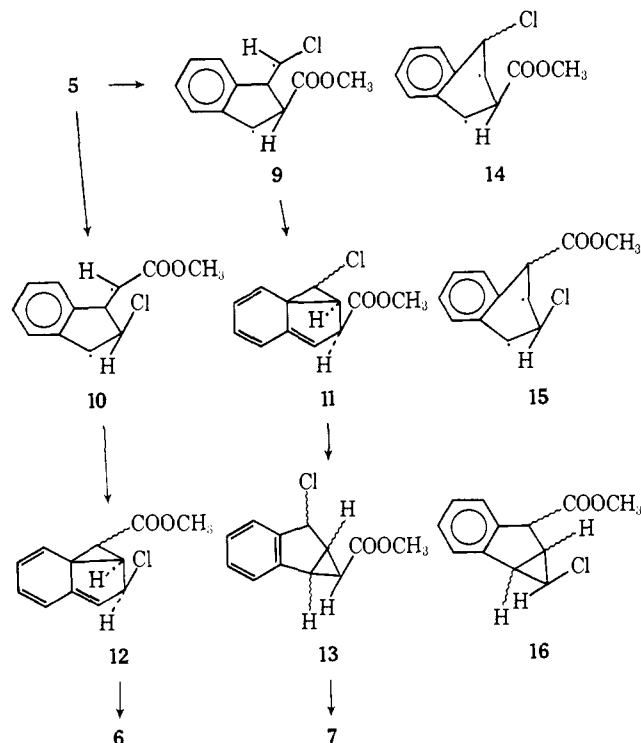
(6) (a) W. G. Woods, *J. Org. Chem.*, **23**, 110 (1958); (b) W. M. Halper, G. Gaertner, E. W. Swift, and G. E. Pollard, *Ind. Eng. Chem.*, **50**, 1131 (1958); (c) J. H. Birely and J. P. Chesick, *J. Phys. Chem.*, **66**, 568 (1962); (d) W. G. Herndon and L. L. Lowry, *ibid.* **68**, 1922 (1964).

(7) (a) R. K. Hill and R. M. Carlson, *J. Org. Chem.*, **30**, 2414 (1965); (b) S. J. Cristol and R. Caple, *ibid.*, **31**, 585 (1966); (c) M. Pomerantz and G. W. Gruber, *ibid.*, **33**, 4501 (1968).

(8) F. T. Bond and L. Scerbo, *Tetrahedron Lett.*, 2789 (1968).

same temperature which, in turn, was some 170–220° lower than that necessary for benzonorbornadiene. The greater reactivity of **1** as compared to benzonorbornadiene is probably due to increased strain.

Combined with the related known reactions, we do consider two alternative rearrangement pathways, both of which involve initial cleavage of the C(1)–C(2) and/or C(1)–C(8) bonds to form the diradicals **9** and **10**. The rate enhancement with the introduction of the chloro or the carbomethoxyl group can be ascribed to the well-known stabilization effect of these substituents on a radical.[9] Smallness or absence of the effect of the disub-

stitution on rate, relative to the monosubstitution, indicates that the cleavages of C(1)–C(2) and C(1)–C(8) bonds are independent of each other, in other words, cleavage of one bond is not influenced by a substituent on the other bond. The positive entropy of activation observed supports an increase in the freedom of motion, as visualized in the transition state leading to the diradicals from the compact 1,3-methanoindan system. The radicals, **9** and **10**, add to the benzene ring to form **11** and **12**, respectively, the former of which transforms into **13** by a vinylcyclopropane–cyclopentene rearrangement restoring the aromatic ring. An analogous transformation of the unsubstituted parent compound of **11** into **2** was proposed by Pomerantz[10] and Meinwald[11] in the study of photolysis of o-divinylbenzene. The presence of such a good leaving group as the chloro at the position of cyclopropylcarbinyl and benzylic characters would lead **13** to **7**. In a similar view the chloro group in **12** is also reactive, so that a facile conversion of **12** into a naphthalene derivative **6** is very likely.

Alternatively, 1,2-aryl rearrangements in **9** and **10** yield the diradicals **14** and **15**, respectively. A number of 1,2-aryl migrations in the radical reactions have been

(9) Refer to C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p 51.
(10) M. Pomerantz, *J. Amer. Chem. Soc.*, **89**, 694 (1967).
(11) J. Meinwald and P. H. Mazzocchi, *ibid.*, **89**, 696 (1967).

known[12] and the transformation of primary radicals into secondary radicals as considered here should be preferred. Directly from **14** and **15** or through the intermediates **13** and **16**, the formation of **6** and **7** is conceivable. These radical pathways are consistent with the absence of a significant solvent effect on the reaction (Table II).

Table II. Solvent Effects on the Rate of **5**

Solvent and composn (v/v)	Temp, °C	$k_1 \times 10^5$, sec^{-1}
CCl₄-pyridine (91:9)	150	7.33
CCl₄-methanol (80:20)	150	7.30
Cyclohexene	150	7.11
No solvent, under vacuum	150	7.80
Dioxane	160	17.2
Dioxane, under N₂	160	17.2

It would be of current interest to attempt rationalization of the present results in terms of orbital symmetry rules.[13] In fact, a suprafacial [1,3]-sigmatropic rearrangement was suggested for the thermal isomerization of bicyclo[2.1.1] hex-2-ene to bicyclo[3.1.0] hex-2-ene by Masamune, et al.,[14] who found the stereospecific migration of the exo-5-acetoxyl substituent in the [2.1.1] system to the exo-6 position in the [3.1.0] system. If the present reaction belongs to the same category, an endo-2-substituted 1,3-methanoindan should form stereospecifically the two intermediates **17** and **18**, by initial cleavage of the C(1)–C(2) and C(1)–C(8) bonds, respectively, as illustrated in the following chart.[15,16] Then, if the second step, the vinylcyclopropane to cyclopentene rearrangement, is concerted (less likely[17]), **17** and **18** should form only two products, 1 and 6 derivatives of **2**, in which the substituents at C-1 and C-6 are attached stereospecifically. On the other hand, if it is not concerted (more likely[17]), such a stereospecific orientation of the substituents would not be expected. With hopes of obtaining information on this point, we carefully followed the reaction of methyl 1,3-methanoindan-endo-2-carboxylate (**19**) by using capillary vpc and nmr spectroscopy. The vpc indicated a complex mixture of products (not less than seven peaks). The nmr did not show signals expected for a cyclopropyl ring, but vinyl

(12) W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 266–273.
(13) For example, see J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).
(14) S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Amer. Chem. Soc.*, **91**, 4322 (1969). We thank Professor Masamune for showing us their preprint.
(15) The signs of the highest occupied orbitals were determined in view of the intermediates being analogs of the benzyl radicals and o-xylylene. For the coefficient values, see C. A. Coulson and S. Streitwieser, Jr., "Dictionary of π-Electron Calculations," Pergamon Press, Inc., Oxford, 1965, pp 106, 186.
(16) It was pointed out by a referee that the substituent effects on rate (Table I) are compatible with both the aforementioned biradical mechanisms and this concerted mechanism, since one of the resonance forms of the transition state for the concerted reaction will resemble the diradical.
(17) The authors learned from a referee of instructive lectures of W. von E. Doering and R. Hoffmann at the 21st National Organic Chemistry Symposium of the American Chemical Society, Salt Lake City, Utah, June 15–19, 1969, which was held after the authors submitted this paper. Doering has stated that, at least in the case of the racemization to thujene, the vinylcyclopropane to cyclopentene rearrangement is not concerted. According to Hoffmann, the rearrangement is a thermally allowed σ2a + π2s or σ2s + π2a cycloaddition, and with the constraints imposed by the bicyclo[3.1.0]hexene ring system could not, on steric grounds, be concerted.

19, X = COOCH₃

17

6-substituted 2

1-substituted 2

18
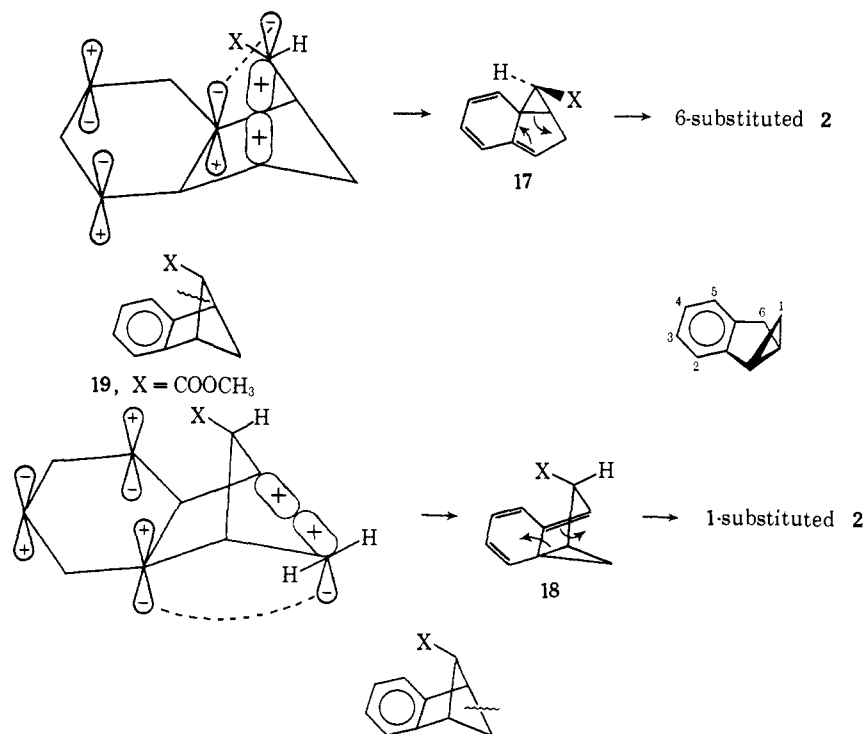
protons. Thus we failed in the attempt to obtain derivatives of **2** and to investigate orientations of the carboxyl groups. Further studies with other kinds of proper monosubstituted 1,3-methanoindans are necessary.

Experimental Section

Methyl *anti*-**2-Bromo-1,3-methanoindan-*exo*-8-carboxylate.** Essentially the same reaction route as used for **5**[4] was applied for the synthesis, starting from *anti*-9-bromobenzonorbornen-*exo*-2-ol which was obtained by the addition of hypobromous acid to benzonorbornadiene: mp 82.5–83.5°; $\nu_{max}^{CCl_4}$ 1738 (s), 1460 (w), 1448 (w), 1436 (m), 1342 (w), 1250 (s), 1219 (m), 1200 (m), 1195 (w), 1037 (m), and 1005 cm⁻¹ (w). *Anal.* Calcd for $C_{12}H_{11}O_2Br$: C, 53.96; H, 4.15; Br, 29.91. Found: C, 54.11; H, 4.20; Br, 30.11.

Physical properties of the intermediates on the synthetic route are as follows.

anti-9-Bromobenzonorbornen-*exo*-2-ol had mp 96.5°; $\nu_{max}^{CCl_4}$ 1461 (m), 1411 (m), 1226 (s), 1155 (w), 1091 (m), and 1058 cm⁻¹ (s). *Anal.* Calcd for $C_{11}H_{11}OBr$: C, 55.25; H, 4.64. Found: C, 55.25; H, 4.60.

anti-9-Bromobenzonorbornen-2-one had mp 55–56°; $\nu_{max}^{CCl_4}$ 1794 (w), 1759 (s), 1459 (m), 1405 (w), 1240 (m), and 1079 cm⁻¹ (m).

anti-9-Bromobenzonorbornene-2,3-dione had mp 148°; $\nu_{max}^{CCl_4}$ 1783 (s), 1765 (s), 1462 (m), 1213 (m), and 1093 cm⁻¹ (m). *Anal.* Calcd for $C_{11}H_7O_2Br$: C, 52.62; H, 2.81; Br, 31.83. Found: C, 52.30; H, 2.82; Br, 31.70.

Rate Measurements. The rates of thermolysis of the carboxylates were determined up to 30–70% completion following the intensity change of the carbonyl stretching bands. The bands were 1740 cm⁻¹ for **5**, 1743 for **8**, 1728 for methyl 1,3-methanoindan-*endo*-2-carboxylate (**19**), and 1738 for methyl *anti*-bromo-1,3-methanoindan-*exo*-2-carboxylate. The intensities were corrected for overlapping with bands of the products. The rates of **1**, **3**, and **8** were determined by decreasing peak areas on vpc due to the reactants. Internal references used were biphenyl, β-methylnaphthalene, and naphthalene. No discrepancy beyond experimental errors was observed between the data from infrared and those from vpc.