[Contribution from Frick Chemical Laboratory, Princeton University]

Aryl Norbornane Derivatives. I. Preparation of Compounds[1,2]

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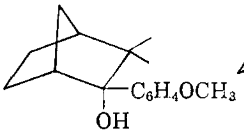
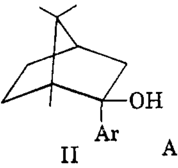
The preparation by standard methods of a number of 1-aryl, 2-aryl and 1,2-diarylnorbornane derivatives desired for physical organic investigations is reported (Chart I). The key step was the Wagner-Meerwein rearrangement of 2-aryl-2-*endo*-norbornanols VII to esters of 1-aryl-2-*exo*-norbornanols X in acid media. The structures of the rearranged products were proven by chemical and spectroscopic means. Several incidental observations are described.

Although a number of aryl substituted camphor, fenchone and camphenilone compounds have been reported,[4-8] simple aryl derivatives of bicyclo[2.2.1]heptane have not been thoroughly studied. 5-Phenyl-2-norbornene, the Diels-Alder adduct of styrene and cyclopentadiene, was the first example of this latter type reported.[9] Bruson[10] investigated the hydration of this olefin, but neither the composition nor the structure of the product was established. Saunders and Benjamin[11] have shown recently that the reaction gave a complex mixture of 5- and 6- phenyl-2-norbornanols. 3-Phenyl-2-norbornanone,[12] *exo*-2-phenylnorbornane from the Friedel-Crafts alkylation of benzene with norbornene,[13] 2-*endo*-phenylnorbornane, the major isomer from the hydrogenation of the styrene cyclopentadiene adduct,[11] and 2-*p*-anisyl norbornene, from the action of *p*-anisyl Grignard reagent upon 2-norbornanone,[6] complete the meager list of known compounds pertinent to the present study.

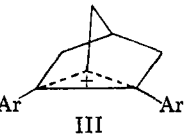
α-Aryl carbonium ions and carbonium ions present in the bicyclo[2.2.1]heptyl ring system are unusually stable. Bartlett conceived the idea of combining these features into a single molecule. Ions obtained from 2-*p*-anisylcamphenilol (I) and related compounds proved to be exceptionally persistent in acid solution; additional observations further strengthened the possibility that these ions possessed bridged, nonclassical structures.[6] Similar results have been obtained by Deno and co-workers with 2-aryl-2-bornanols (II.)[7]



I



II



III

We wished to see whether the presence of a second aryl substituent would give stable ion III. The synthetic route chosen to possible precursors of III (Chart I) gave a series of compounds which were desired for other investigations: π. . . .OH hydrogen bonding[14]; the rates of solvolysis of 1-aryl-2-norbornyl derivatives[2]; and the stabilities and behavior of monoaryl norbornyl carbonium ions, uncomplicated by the presence of methyl groups.[6,7] This paper records the preparation and the structure proofs for the compounds which were employed in these investigations.

RESULTS

2-Norbornanone (VI). Because of the need for large amounts of norbornanone (VI) in this work,

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[1] Paper VI of a series on Bridged Ring Systems· Paper V, P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961). This work is part of the Ph.D. thesis of D. C. K., Princeton University, 1960.

[2] Preliminary accounts of this work were presented at the Third Delaware Valley Regional Meeting, Am. Chem. Soc., Philadelphia, Pa., Feb., 1960, Abstracts, p. 33; and at the 138th National Meeting, American Chemical Society, New York, N. Y., Sept., 1960, Abstracts, p. 43P.

[3] Proctor and Gamble Fellow, 1958–1959. National Science Foundation Summer Fellow, 1959.

[4] The earlier literature has been reviewed: F. Radt and E. Josephy, eds., *Elsevier's Encyclopaedia of Organic Chemistry*, Elsevier, New York, Vol. 12A, 1948; Vol. 13, 1946; J. L. Simonsen, *The Terpenes*, Cambridge University Press, Cambridge, England, Vol. II, Second Ed., 1949; E. R. Webster, Ph.D. thesis, Radcliffe College, 1951.

[5] S. S. Nametkin and T. V. Sheremeteva, *Zhur. Obschei Khim.*, **17**, 335 (1947); S. S. Nametkin and G. A. Serebrennikov, *Zhur. Obschei Khim.*, **15**, 195 (1945), and earlier papers by S. S. Nametkin.

[6] P. D. Bartlett, E. R. Webster, C. E. Dills, and H. G. Richey, Jr., *Ann.*, **623**, 217 (1959); H. G. Richey, Jr., thesis, Harvard University, 1958; P. D. Bartlett, C. E. Dills, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **82**, 5414 (1960).

[7] (a) N. C. Deno, P. T. Groves, J. J. Jaruzelski, and M. N. Lugasch, *J. Am. Chem. Soc.*, **82**, 4719 (1960); (b) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044 (1955).

[8] (a) A. N. Nesmeyanov, V. A. Sazonova, and R. G. Materikova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk.* 998 (1955); (b) H. Rupe and R. Hagenbach, *Helv. Chim. Acta*, **28**, 81 (1945); M. Lipp and D. Bernstein, *Naturwissenschaften*, 42, 578 (1955).

[9] K. Alder and H. F. Rickert, *Ber.*, **71**, 373 (1938).

[10] H. A. Bruson, U. S. Patent, **2,426,725**, Sept. 2, 1947 [*Chem. Abstr.*, **42**, 215 (1948)].

[11] Unpublished results, personal communications from W. H. Saunders, Jr. (We abandoned attempts to use this route for preparative purposes when the complexity of the hydration product became apparent.)

[12] W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952).

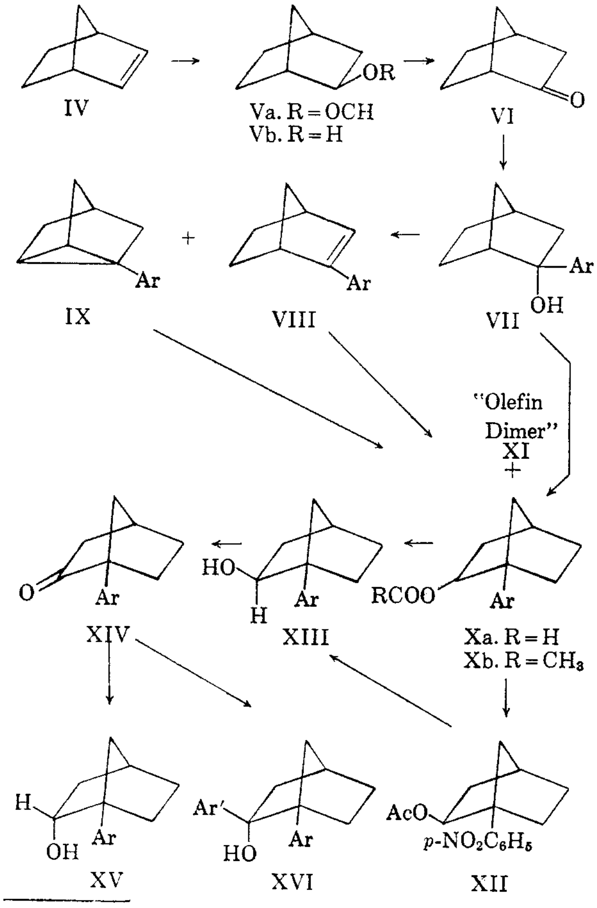
[13] L. Schmerling, U. S. Patent **2,480,267**, Aug. 30, 1949 [*Chem. Abstr.*, **44**, 1136 (1950)].

[14] P. Von R. Schleyer, C. Wintner, D. S. Trifan, and R. Bacskai, *Tetrahedron Letters*, No. 14, 1 (1959).

an expeditious two-step preparation from norbornene (IV)[15] was developed. Formic acid of 98–100% concentration adds readily to the strained double bonds of bicyclo[2.2.1]heptene derivatives.[16] Norbornene (IV) gave over 90% yield of 2-*exo*-norbornyl formate (Va). No catalyst was needed.[17] Advantage was taken of the observation of Corey and co-workers that formate esters of secondary alcohols can be oxidized directly to ketones.[18] Chromic acid–acetone oxidation[19] of Va gave 2-norbornanone in 85% yield. This method obviates the necessity of preparing 2-*exo*-norbornanol (Vb) and is superior to the traditional synthesis of this compound.[20]

Chart I

Synthesis of Aryl Bicyclo[2.2.1]heptane Derivatives



2-Aryl-2-endo-norbornanols (VII) *and their dehydration.* The literature records the addition of aryl Grignard[4-7] and aryllithium[8] reagents to a number of bicyclo[2.2.1]heptan-2-ones, but only one such addition to 2-norbornanone itself.[6] Table I lists the 2-aryl-2-*endo*-norbornanols (VII) prepared in the present work. Phenyllithium was employed in the preparation of VII (Ar = C_6H_5). An *n*-butyllithium interchange with *p*-bromo-*N*,*N* dimethylaniline[21] was used in the synthesis of VII (Ar = *p*-$(CH_3)_2NC_6H_4$). The other alcohols were obtained through the corresponding Grignard reagents.

The stereochemical assignment of these alcohols—aryl group, *exo;* hydroxyl, *endo*—was made by analogy to the known course of methyl Grignard additions to 2-norbornanone and to 5-norbornen-2-one.[22] This assignment is consistent with the "rule of *exo*-addition" to norbornane compounds with no *syn*-7-substituents[23] and with the course of metal hydride reductions of 2-norbornanones.[24]

In one preparation of 2-*p*-anisyl-2-*endo*-camphenilol (VII. Ar = *p*-$CH_3OC_6H_4$) the product was overheated prior to distillation. Olefin VIII (Ar = *p*-$CH_3OC_6H_4$) of melting point identical with the literature value[6] was produced. The *o*-anisyl and *p*-tolyl alcohols could be dehydrated similarly; potassium bisulfate was used as a catalyst for the other compounds. The dehydration products are probably all mixtures of olefin VIII and nortricyclene derivative IX. The presence of about 20% 1-phenylnortricyclene (IX. Ar = C_6H_5) in the dehydration product of VII (Ar = C_6H_5) was established by oxidative removal of olefin VIII (Ar = C_6H_5) and comparison with an authentic sample.[25] VII (Ar = *p*-$CH_3OC_6H_4$), dehydrated thermally,[6] gave a solid product which took up 92% of the theoretical amount of hydrogen.[6] This suggests that the mixture contained about 8% IX (Ar = *p*-$CH_3OC_6H_4$). The formation of tricyclic byproducts during the dehydration of bicyclo[2.2.1]heptyl alcohols is extremely common.[4-6] The parent olefin, norbornene (IV) is actually less stable thermodynamically than nortricyclene (IX. Ar = H), but substituents reverse this stability order.[26]

Ultraviolet data for the olefins VIII are given in Table II. No correction in the extinction coefficients has been made because of the presence of

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[15] J. Meinwald and N. J. Hudak, *Org. Syntheses*, **37**, 65 (1957).

[16] *Cf.* dicyclopentadiene: F. Bergmann and H. Japhe, *J. Am. Chem. Soc.*, **69**, 1826 (1947); *Anal. Chem.*, **20**, 146 (1948).

[17] L. Schmerling, J. P. Luvisi, and R. W. Welch, *J. Am. Chem. Soc.*, **78**, 2819 (1956) reported the boron fluoride etherate catalyzed addition of 88% formic acid to norbornene. Ester yield was 71%.

[18] E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *J, Am. Chem. Soc.*, **81**, 6503 (1959).

[19] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch, and G. W. Wood, *J. Chem. Soc.*, 2402 (1952).

[20] K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1940).

[21] H. Gilman and J. Banner, *J. Am. Chem. Soc.*, **62**, 344 (1940).

[22] S. Beckmann, R. Schaber, and R. Bamberger, *Ber.*, **87**, 997 (1954); N. J. Toivonen, E. Siltanen, and K. Ojala, *Ann. Acad. Sci. Fenn.*, AII, No. 64 (1955); N. J. Toivonen, XIV Int. Cong. Pure Appl. Chem., Zurich, Switzerland, July, 1955, Abstracts, p. 45.

[23] K. Alder, G. Stein, and H. F. Rickert, *Ann.*, **525**, 221 (1956) and many subsequent examples.

[24] S. Beckmann and R. Mezger, *Ber.*, **89**, 2738 (1956); P. Hirsjärvi, *Ann. Acad. Sci. Fenn.*, AII, No. 81 (1957).

[25] D. C. Kleinfelter and Paul von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 2329 (1961).

[26] Paul von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958).

nortricyclene IX. The presence of these impurities probably does not affect appreciably the position of the maxima since 1-phenylnortricyclene (IX) absorbed at a much shorter wave length (λ_{max} 226 mμ, log ϵ 3.92) than 2-phenylnorbornene (VIII. Ar = C_6H_5).[25] Substituents on the benzene ring have a similar effect upon the position of the maxima in the 2-arylnorbornene and in the styrene series.[27,28]

TABLE I

Preparation of 2-Aryl-2-*endo*-norbornanols (VII) and Derivatives

VII, Ar	Average Yield, %	M.P. B.P.	Empirical Formula	Carbon, %		Hydrogen, %		X, %		M.P. of PNB Deriv.[b]	Empirical Formula	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found			Calcd.	Found	Calcd.	Found
C_6H_5	77.4	44.2–44.6 158–168$_{17-18}$	$C_{13}H_{16}O$	82.93	82.69	8.57	8.54	—	—	136.1–136.4	$C_{20}H_{19}O_4N$	71.20	71.36	5.68	5.63
										(71.2–72.0)[c]	$C_{15}H_{18}O_2$	78.23	78.10	7.88	8.10
p-$CH_3C_6H_4$	71.6[a]	135–150$_{2.0-2.5}$								140–141 dec.	$C_{21}H_{21}O_4N$	71.78	71.48	6.02	6.08
								Chlorine							
p-ClC_6H_4	77.7	85.9–86.3 187–195$_{15}$	$C_{13}H_{15}OCl$	70.11	69.94	6.79	6.71	15.92	15.63	127.6–128.5	$C_{20}H_{18}O_4$-NCl	64.60	64.56	4.88	4.81
o-$CH_3OC_6H_4$	83.5[a]	50.4–51.6 152–160$_{2.7}$	$C_{14}H_{18}O_2$	77.03	76.80	8.31	8.36	—	—	115–116 dec.	$C_{21}H_{21}O_5N$	68.65	68.62	5.76	5.88
m-$CH_3OC_6H_4$	67.3	190–195$_{14}$								123.9–124.3	$C_{21}H_{21}O_5N$	68.65	68.53	5.76	5.95
p-$CH_3OC_6H_4$	82.9[a]	160–170$_{2-2.5}$								90–105 dec.	$C_{21}H_{21}O_5N$	68.65	68.16	5.76	5.80
								Nitrogen							
p-$(CH_3)_2NC_6H_4$	47.3	103.0–103.8	$C_{15}H_{20}ON$	77.88	77.92	9.15	9.32	6.05	6.19	[d]					

[a] In some preparations the alcohol dehydrated slightly during distillation. [b] p-Nitrobenzoate derivative. [c] Acetate derivative. [d] A reaction was observed in the attempted p-nitrobenzoate preparation, but no solid derivative could be isolated.

TABLE II

Ultraviolet Absorption of 2-Aryl Norbornenes (VIII) in Ethanol

Ar	λ_{max}	log ϵ
C_6H_5	262.5	4.03
p-$CH_3C_6H_4$	264	4.08
p-ClC_6H_4	267	4.19
o-$CH_3OC_6H_4$	258	3.88
m-$CH_3OC_6H_4$	259.5	3.98
p-$CH_3OC_6H_4$	268	4.21

Rearrangement to X and formation of "olefin dimer" (XI). VII, VIII and IX should all give the same carbonium ion in acid solution[29]; precedents for the rearrangement of these compounds to X abound in the terpene literature.[4–6] Two of the most widely used media for this purpose were employed here, 98–100% formic acid[10,11,16,17] and acetic acid with 50% sulfuric acid catalyst.[30] As expected, both the alcohols VII and the olefin VIII–nortricyclene IX mixtures gave rearranged esters X when heated in formic acid or in acetic–acid–sulfuric acid solution. However, depending upon the nature of the substituent, varying amounts of higher molecular weight by-products were formed; these corresponded in formula to dimers of olefin VIII (or of nortricyclene IX). Possible structures for these "olefin dimers" XI will be considered below.

Table III summarizes the observations made upon the esters X. The results can be generalized as follows: (1) Greater yields were obtained with the acetic acid–sulfuric acid modification than with formic acid. (2) Olefin starting material appeared to give smaller yields of ester. (3) The presence of electron releasing substituents on the benzene ring decreased the yields of ester and presumably increased the yields of "olefin dimer." Starting material was not recovered. A Hammett plot of the yield data obtained from similar reactions and identical conditions (log yield Xb, Ar = aryl—log yield Xb, Ar = phenyl) gave an excellent[31] correlation with the

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(27) W. H. Saunders, Jr., and R. A. Williams, *J. Am. Chem. Soc.*, **79**, 3712 (1957); J. F. Eastham and D. R. Larkin, *J. Am. Chem. Soc.*, **80**, 2887 (1958).

(28) The influence of ring strain upon λ_{max} of VIII will be discussed in a separate note.

(29) N. C. Deno, P. von R. Schleyer, and D. C. Kleinfelter, *Tetrahedron Letters*, No. 12, 414 (1961).

(30) J. Bertram and H. Walbaum, *J. prakt. Chem.*, [2] **49**, 1 (1894).

(31) According to the definition of H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

TABLE III

PREPARATION OF 1-ARYL-2-*exo*-NORBORNYL ESTERS X

Ar	Average Yield, %	M.P., B.P.	n^{20}_{D}	Empirical Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
C_6H_5 (Xb)	68.0[a]	44.5–45.5		$C_{15}H_{18}O_2$	78.23	78.03	7.88	7.78	—	—
		158–160$_{13}$	1.53163							
(Xa)	35.0[b]	140–180$_{17-18}$	1.54799							
(Xa)	30.0[c]	150–185$_{19}$	1.54914							
p-$CH_3C_6H_4$ (Xb)	38.2[a]	140–150$_{2.5}$	1.53535							
(Xb)	24.3[d]	140–150$_{2.5}$	1.53560							
(Xa)	23.0[b]	160–175$_{14}$	1.54692							
p-ClC_6H_4 (Xb)	88.0[a]	158–170$_{0.7}$	1.54753							
o-$CH_3OC_6H_4$ (Xb)	66.5[a]	147–155$_{0.5}$	1.53632							
(Xb)	39.7[d]	178–188$_{3.0}$	1.53592							
(Xa)	35.8[c]	145–155$_{0.5}$	1.54596							
m-$CH_3OC_6H_3$ (Xb)	71.8[a]	180–192$_{12}$	1.53068							
p-$CH_3OC_6H_4$ (Xb)	9.6[a]	64.2–65.2	—	$C_{16}H_{20}O_3$	73.82	73.76	7.74	7.70	—	—
		138–153$_{1-2}$								
(Xa)	0.0[b]	—	—							
p-$NO_2C_6H_4$ (Xb)	66.2[e]	102.5–103.1	—	$C_{15}H_{17}O_4N$	65.44	65.71	6.22	6.39	5.09	5.13
p-$NH_2C_6H_4$ (Xb)	85.0[e]	101.4–102.0	—	$C_{15}H_{19}O_2N$	73.44	73.52	7.81	8.00	5.71	5.53
p-$(CH_3)_2NC_6H_4$ (Xb)	85.9[e]	87.5–88.0	—	$C_{17}H_{21}O_2N$	74.69	74.48	8.48	8.57	5.12	5.34

[a] Acetic acid procedure from VII. [b] Formic acid procedure from VII. [c] Formic acid procedure from VIII (+IX). [d] Acetic acid procedure from VIII (+IX). [e] Not prepared by rearrangement. See text.

σ^+ substituent constants,[33] but the plot verus σ constants was unsatisfactory.[31,32]

Deno, Graves, and Saines[34] have reported that the formation of dimer from diaryl olefins proceeds most rapidly when the olefin and olefin cation are present in equivalent amounts. In the present case, the results can be explained in terms of competition between olefin and solvent for the intermediate carbonium ion. Olefin dimer is formed in higher percentage from olefin starting material VIII than from alcohol VII. In the latter case carbonium ion formation must precede the production of olefin; ester formation can compete more successfully. No dimer was reported from the action of formic acid on *p*-anisylcamphenilol I.[6] Presumably the *gem*-dimethyl group precludes dimer formation either because of the impossibility of obtaining olefin of type VII or because of steric hindrance. The effects of changes in substituents and of changes in the reaction medium on the yields of ester can be rationalized in several ways, but insufficient information is available to permit distinction between the mechanistic possibilities.

The nitrogen containing compounds (Xb. Ar = *p*-$NO_2C_6H_4$; *p*-$NH_2C_6H_4$; and *p*-$(CH_3)_2NC_6H_4$) were not prepared by a rearrangement sequence. Direct nitration[35] of 1-phenyl-2-*exo*-norbornyl acetate (Xb. Ar = C_6H_5) gave *para* product, XII.[36] Catalytic reduction of the nitro compound gave the aniline derivative Xb (Ar = *p*-$NH_2C_6H_4$,)[37] while reductive alkylation[38] produced Xb (Ar = $(CH_3)_2NC_6H_4$) directly.

When 1-phenyl-2-*exo*-norbornanol (see experimental) was nitrated by the same procedure, the product had the correct properties for 1-*p*-nitrophenyl-2-*exo*-norbornyl nitrate XVII. Toivonen has shown that *exo* alcohols in the bicyclo[2.2.1]heptane series react with nitric acid to give nitrate esters while *endo* alcohols are oxidized to ketones under the same conditions.[39]

Friedel-Crafts acylation of the phenyl derivative Xb (Ar = C_6H_5) with acetic anhydride and aluminum chloride was attempted. The product was obviously not the acetophenone derivative Xb (Ar = *p*-$CH_3COC_6H_4$). Acetate bands were lacking in the infrared spectrum, and the position of the ultraviolet maximum, 272 mμ (log ε 3.83), indicated a degree of conjugation similar to *cis*-benzalacetone (λ_{max} 280 mμ, log ε 4.00)[40] rather than to 4-methylacetophenone (λ_{max} 243 mμ, log ε 4.12).[41] The in-

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[32] This correlation is indicative but not strictly correct; see O. Exner, *Coll. Czech. Chem. Comm.*, **26**, 1 (1961). Use of the relationships proposed by Exner does not lead to linear plots with either σ or σ^+ constants.

[33] Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

[34] N. C. Deno, P. T. Graves, and G. Saines, *J. Am. Chem. Soc.*, **81**, 5790 (1959).

[35] The procedure was that used by R. A. Sneen, *J. Am. Chem. Soc.*, **80**, 3971 (1958).

[36] *Cf.*, the nitration of *t*-butylbenzene. H. Cohn, E. D. Hughes, M. H. Jones, and M. G. Peeling, *Nature*, **169**, 291 (1952); L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 5621 (1959).

[37] *Cf.*, R. Adams and F. L. Cohen, *Org. Syn.*, Coll. Vol. 1, 240 (1941).

[38] R. E. Bowman and H. H. Stroud, *J. Chem. Soc.*, 1342 (1950).

[39] H. Toivonen, *Suom. Kemistilehti*, **B25**, 69 (1952); **B26**, 75 (1953); *Ann. Acad. Sci. Fennicae*, AII, No. 72 (1956).

[40] G. Gamboni, V. Theus and H. Schinz, *Helv. Chim. Acta*, **38**, 255 (1955).

[41] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

TABLE IV

PREPARATION OF 1-ARYL-2-*exo*-NORBORNANOLS, XIII

Ar	Average Yield, %	M.P. B.P.	Empirical Formula	Carbon, %		Hydrogen, %		X, %		M.P. of PNB Deriv.[c]	Empirical Formula	Carbon, %		Hydrogen, %		X, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found			Calcd.	Found	Calcd.	Found	Calcd.	Found
C_6H_5	96.4	69.5–70.0 $158–164_{17-18}$	$C_{13}H_{16}O$	82.93	82.79	8.57	8.45			148.6–149.4	$C_{20}H_{19}O_4N$	71.20	71.40	5.68	5.69		
p-$CH_3C_6H_4$	89.0	60.1–60.7	$C_{14}H_{18}O$	83.12	83.08	8.97	8.77			122.9–123.5	$C_{21}H_{21}O_4N$	71.78	71.59	6.02	6.11		
p-ClC_6H_4	95.3	68.4–69.2 $175–183_{6.0-7.5}$	$C_{13}H_{15}OCl$	70.11	70.21	6.79	6.79	Chlorine 15.92	16.04	125.6–126.3	$C_{20}H_{18}O_4NCl$	64.60	64.49	4.88	4.96	Chlorine 9.54	9.31
o-$OCH_3C_6H_4$	*ca.* 100	63.3–64.1	$C_{14}H_{18}O_2$	77.03	76.90	8.31	8.19			87.0–87.5	$C_{21}H_{21}O_5N$	68.65	68.54	5.76	5.72		
m-$OCH_3C_6H_4$	94.2	$180–185_{12}$	(n_D^{20} 1.55411, 1.5561)							104.4–105.1	$C_{21}H_{21}O_5N$	68.65	68.47	5.76	5.91		
p-$OCH_3C_6H_4$	*ca.* 100	52.8–53.8	$C_{14}H_{18}O_2$	77.03	76.84	8.31	8.43			116.1–116.8	$C_{21}H_{21}O_5N$	68.65	68.95	5.76	5.90		
p-$NO_2C_6H_4$	87.5	147.4–148.0	$C_{13}H_{15}O_3N$	66.93	66.68	6.48	6.50	Nitrogen 6.01	6.07	196.7–197.2	$C_{20}H_{18}O_6N_2$	62.82	62.60	4.75	4.74	Nitrogen 7.33	7.38
p-$NH_2C_6H_4$	83.2[a] 94.7	111.2–111.7	$C_{13}H_{17}OH$	76.81	76.64	8.43	8.53	6.89	6.91								
p-$N(CH_3)_2C_6H_4$	88.2	114.0–114.4	$C_{15}H_{21}ON$	77.88	77.59	9.15	9.12	6.05	5.96	145.9–146.6[b]	$C_{22}H_{24}O_4N_2$	69.45	69.59	6.36	6.65	Nitrogen 7.36	7.60

[a] Brick-red solid; pale yellow in ethanol solution. [b] Prepared from the nitro acetate by the procedure of M. S. Dewar and T. Mole, *J. Chem. Soc.*, 2556 (1956). *l* *p*-Nitrobenzoate derivative.

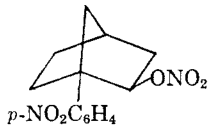
TABLE V

PREPARATION OF 1-ARYL-2-NORBORNANONES, XIV

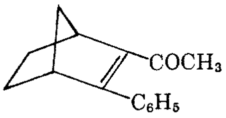
Ar	Average Yield, %	M.P. B.P.	Empirical Formula	Carbon, %		Hydrogen, %		X, %		M.P. of 2,4-DNP Deriv.[c]	Empirical Formula	Carbon, %		Hydrogen, %		X, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found			Calcd.	Found	Calcd.	Found	Calcd.	Found
C_6H_5	51.3	40.2–41.0 $161–168_{14}$	$C_{13}H_{14}O$	83.83	84.00	7.58	7.64			209.6–210.6	$C_{19}H_{18}O_4N_4$	62.28	62.52	4.95	5.23	Nitrogen 15.29	15.50
p-$CH_3C_6H_5$	68.5	86.4–86.8	$C_{14}H_{16}O$	83.96	83.76	8.05	8.01			190.3–190.6	$C_{20}H_{20}O_4N_4$	63.15	63.00	5.30	5.35		
p-ClC_6H_4	66.3	77.0–77.7	$C_{13}H_{13}OCl$	70.75	70.90	5.94	6.06	Chlorine 16.07	16.00	209.5–210.0	$C_{19}H_{17}O_4N_4Cl$	56.93	56.80	4.28	4.36	Chlorine 8.85	8.71
o-$OCH_3C_6H_4$	59.6	95.1–95.6	$C_{14}H_{16}O_2$	77.75	77.59	7.46	7.47			201.6–202.2	$C_{20}H_{20}O_5N_4$	60.60	60.31	5.09	5.27		
m-$OCH_3C_6H_4$	70.5	$135–145_{0.7-1.0}$								193.2–193.9	$C_{20}H_{20}O_5N_4$	60.60	60.44	5.09	5.11		
p-$OCH_3C_6H_4$	62.3	100.4–101.4	$C_{14}H_{16}O_2$	77.75	77.65	7.46	7.53			208.3–208.7	$C_{20}H_{20}O_5N_4$	60.60	60.37	5.09	5.25		
p-$NO_2C_6H_4$	73.5	124.6–125.2	$C_{13}H_{13}O_3N$	67.52	67.60	5.67	5.86	Nitrogen 6.06	6.08	233.0–233.8	$C_{19}H_{17}O_6N_5$	55.47	55.31	4.17	4.33	Nitrogen 17.03	16.97
p-$NH_2C_6H_4$[a,b]	88.8	175.8–176.7	$C_{13}H_{15}ON$	77.58	77.48	7.51	7.69	6.96	7.14								
p-$N(CH_3)_2C_6H_4$[a]	76.8	90.8–91.4	$C_{15}H_{19}ON$	78.56	78.40	8.35	8.30	6.11	6.28								

[a] Prepared from XIV (Ar = *p*-$NO_2C_6H_4$) by reductive processes. See Experimental. [b] Also produced in 21.4% yield by Oppenauer oxidation of 1-*p*-aminophenyl-2-*exo*-norbornanol. [c] 2,4-Dinitrophenylhydrazone derivative.

frared spectrum possessed bands characteristic of a conjugated carbonyl group (1655 cm.$^{-1}$) and a monosubstituted benzene ring (742 and 697 cm.$^{-1}$).[42] The structure, 3-acetyl-2-norbornene (XVIII), was assigned to this product. It evidently arose by the following sequence: loss of the elements of acetic acid from Xb (Ar = C_6H_5) with rearrangement gave 2-phenylnorbornene (VIII. Ar = C_6H_5) under the reaction conditions. Friedel-Crafts alkene acylation of this olefin yielded XVIII.[43]



XVII

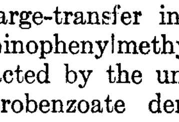


XVIII

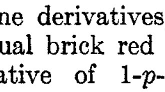
1-Aryl-2-exo-norbornanols (XIII) *and their oxidation.* Saponification of the 1-aryl-2-norbornyl esters X gave high yields of the 1-aryl-2-*exo*-norbornanols XIII. An acid hydrolysis procedure proved superior to saponification for the *p*-nitro compound XIII (Ar = *p*-$NO_2C_6H_4$).[44] Most of the alcohols were solids; additional characterization as the *p*-nitrobenzoates is recorded in Table IV.

Because of recent interest in the intramolecular charge-transfer interactions in 4-nitrophenyl, 4′-aminophenylmethylene derivatives,[45] we were attracted by the unusual brick red color of the *p*-nitrobenzoate derivative of 1-*p*-dimethylaminophenyl-2-*exo*-norbornanol X (Ar = *p*-$(CH_3)_2NC_6H_4$; R = *p*-$NO_2C_6H_4$). The derivative of the corresponding *endo* alcohol XV (Ar = *p*-$(CH_3)_2NC_6H_4$) was a yellow-orange solid. Solutions of these compounds were pale yellow; their ultraviolet spectra were identical with the spectra of solutions of 1-ethyl-2-*exo*- and 1-ethyl-2-*endo*-norbornanol *p*-nitrobenzoates. Therefore, the inter- or intramolecular forces which were responsible for the dark color of the solids did not persist in solution.

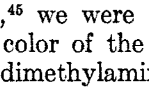
The oxidation of the secondary alcohols XIII to the ketones XIV proceeded smoothly but despite the use of mild conditions[19] the yields seldom exceeded 70% (Table V). Workup of the basic extracts of several preparations gave small amounts of acidic materials. Solid acids were obtained only from the oxidations of the *p*-tolyl and *p*-chlorophenyl alcohols XIII. The melting point ranges were wide and could be but little improved by recrystallization.



XIX



XX



XXI

Mosher and Langerak have reported the isolation of a small amount of α-campholenic acid (XX) from the oxidation of isoborneol (XIX.)[46] If a similar reaction course were to be followed in the present series, the by-product acid would have structure XXI, two double bond isomers being possible. Support for this possibility is afforded by elemental analysis, by neutralization equivalent and by ultraviolet spectroscopy (Table VI).

TABLE VI

ULTRAVIOLET SPECTRA OF SOME ARYL-CONJUGATED OLEFINS

Compound	λ_{max}, mμ	Log ε
1-Phenylcyclopentene	254	4.10
XXI (Ar = *p*-ClC_6H_4)	261	4.28
XXI (Ar = *p*-$CH_3C_6H_4$)	258	*ca.* 4.0
Styrene[27]	248	4.14
p-Chlorostyrene[27]	253	4.29
p-Methylstyrene[27]	252	4.23

Additions to 1-aryl-2-norbornanones. Alcohols XV *and* XVI. Lithium aluminum hydride reduction of the 1-aryl-2-norbornanones XIV proceeded smoothly. The products, even after several recrystallizations, had 2–5° melting-point ranges, indicating the presence of appreciable amounts of *exo* alcohols XIII in the predominantly *endo* XV products. Studies of the stereochemistry of complex hydride reductions of analogous ketones have shown *endo:exo* ratios of more than 9:1.[24] Sodium borohydride reduction appeared to improve the stereoselectivity in several instances; this reducing agent was the only one used for the *p*-anisyl ketone. Sharp-melting derivatives were obtained in each case (Table VII).

Because of the adverse steric influence of the 1-aryl group, satisfactory preparation of the 1,2-diaryl-2-norbornanols XVI from the 1-aryl-2-norbornanones XIV could not be accomplished by the Grignard procedure. Low yields have been reported in similar cases.[4–7]

Aryllithium reagents gave generally good yields[8] of the desired 1-aryl-2-aryl′-2-*endo*-norbornanols XVI (Table VIII). The stereochemical assignments can be justified by the arguments given earlier.

The action of acetic acid–sulfuric acid[29] upon 1,2-diphenyl-2-*endo*-norbornanol (XVI. Ar = Ar′ = C_6H_5) was studied because of an interest in the course of reactions of 1,2-disubstituted norbornyl derivatives.[47] Tertiary *exo*-acetate, the expected product from the bridged ion intermediate, would be too reactive to be stable under these conditions.

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[42] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, Second Edition, 1958.

[43] G. Langois, *Compt. rend.*, **168**, 1052 (1919).

[44] G. Davies and D. P. Evans, *J. Chem. Soc.*, 339 (1940); H. A. Smith and J. H. Steele, *J. Am. Chem. Soc.*, **63**, 3466 (1941); V. C. Haskell and L. P. Hammett, *J. Am. Chem. Soc.*, 71, 1284 (1949).

[45] W. N. White, *J. Am. Chem. Soc.*, **81**, 2912 (1959).

[46] W. A. Mosher and E. L. Langerak, *J. Am. Chem. Soc.*, **73**, 1302 (1951).

[47] P. Von R. Schleyer, Ph.D. thesis, Harvard University, 1956, pp. 241–248. *Cf.*, H. Toivonen, *Suom. Kemistilehti*, **33B**, 66 (1960).

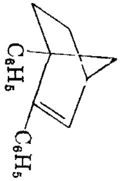
TABLE VII

PREPARATION OF 1-ARYL-2-*endo*-NORBORNANOLS, XV

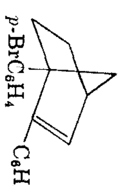
Ar	Average Yield, %	M.P. B.P.	Empirical Formula	Carbon, %		Hydrogen, %		X, %		M.P. of PNB Deriv.^{d}	Empirical Formula	Carbon, %		Hydrogen, %		X, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found			Calcd.	Found	Calcd.	Found	Calcd.	Found
C_6H_5	*ca.* 100^a	69.2–70.0	$C_{13}H_{16}O$	82.93	82.91	8.57	8.62			135.4–136.0	$C_{20}H_{19}O_4N$	71.20	70.92	5.68	5.80		
p-$CH_3C_6H_4$	95.6^a	61.8–62.8	$C_{14}H_{18}O$	83.12	82.97	8.97	8.99			98.9–99.5	$C_{21}H_{21}O_4N$	71.78	71.59	6.02	6.11		
		$125–129_{0.7–0.8}$						Chlorine								Chlorine	
p-ClC_6H_4	97.4^a	54.2–59.2	$C_{13}H_{15}OCl$	70.11	69.87	6.79	6.63	15.92	15.73	98.9–99.5	$C_{20}H_{18}O_4NCl$	64.60	64.78	4.88	5.07	9.54	9.55
	95.3^b	$145–150_{0.7}$															
o-$CH_3OC_6H_4$	85.0^a	41–48								116.1–117.0	$C_{21}H_{21}O_5N$	68.65	68.77	5.76	6.04		
	92.4^b	$144–147_{1.5}$															
m-$CH_3OC_6H_4$	*ca.* 100^a	$132–144_{0.5–1.0}$								87.9–88.6	$C_{21}H_{21}O_5N$	68.65	68.70	5.76	5.98		
p-$CH_3OC_6H_4$	89.6^b	55.6–58.6								125.3–126.2	$C_{21}H_{21}O_5N$	68.65	68.46	5.76	5.87		
								Nitrogen								Nitrogen	
p-$NO_2C_6H_4$	99.5^b	119.1–119.6	$C_{13}H_{15}O_3N$	66.95	66.76	6.48	6.56	6.01	5.81	161.6–162.4	$C_{20}H_{18}O_6N_2$	62.82	62.76	4.75	5.03	7.33	7.18
p-$NH_2C_6H_4$	94.0^c	97.2–97.8	$C_{13}H_{17}ON$	76.81	76.72	8.43	8.48	6.89	7.01	—	—	—	—	—	—	—	—
p-$N(CH_3)_2C_6H_4$	88.0^c	113.2–114.0	$C_{15}H_{21}ON$	77.88	77.62	9.15	9.29	6.05	5.96	138.6–139.1	$C_{22}H_{24}O_4N_2$	69.45	69.10	6.36	6.44	7.36	7.47

^{a} Lithium aluminum hydride reduction. ^{b} Sodium borohydride reduction. ^{c} Prepared from XV (Ar = p-$NO_2C_6H_4$). See Experimental. ^{d} p-Nitrobenzoate derivative.

endo-Acetate,[47] a second possibility, would also be highly reactive because of the phenyl substituent. The reaction product was 1,2-diphenylnorbornene (XXII); the structure was established by spectral methods. Bromination of the same alcohol XVI (Ar = Ar′ = C_6H_5) also gave dehydration. The product was tentatively identified as 1-p-bromophenyl-2-phenylnorbornene (XXIII).



XXII



XXIII

Structure proofs of the rearranged compounds X–XVI. Due to the nature of the investigations to be performed on these arylnorbornyl derivatives it was necessary to verify the positions of the aryl and the ester groups in the Wagner-Meerwein rearrangement products X. Numerous precedents for this transformation exist.[4–6,22,48] Here follows a list of observations related to the structure of esters X and products derived from them by preparative reactions ordinarily free from complication.

1. Intramolecular hydrogen bonding studies[1] on alcohols XIII and XV as well as kinetic investigations on tosylate derivatives of the same alcohols[2] strongly support the assigned structures. Shown clearly is that all of the alcohols of a given type, XIII or XV, correspond to the same series. Chemical interrelation of the different aryl derivatives was not considered to be necessary. All the rearrangement products have the same carbon skeleton.

2. Alkaline permagnate oxidation of 1-phenyl-2-norbornanone (XIV. Ar = C_6H_5) gave an acid substance which had the correct neutralization equivalent and elemental analysis for 1-phenyl-*cis*-1,3-cyclopentanedicarboxylic acid (XXIV) or an isomer. All of the ketones XIV possessed an "adjacent methylene" (—CH_2—CO—) absorption band[18,25,42] in the 1400–1410-cm.$^{-1}$ CH deformation region of the infrared. This evidence establishes the presence of a —CH_2—CO— group and rules out a 3-phenyl ketone structure. The 3-phenyl-2-norbornanone of Wildman and Hemminger.[12] which did not possess a 1400–1440-cm.$^{-1}$ band,[25] was different from ketone XIV (Ar = C_6H_5).

3. Wolff-Kishner reduction of 1-phenyl-2-norbornanone (XIV. Ar = C_6H_5) gave a hydrocarbon, presumably 1-phenylnorbornane (XXV. R = C_6H_5), different from the known 2-*exo*-phenylnorbornane[13] and 2-*endo*-phenylnorbornane.[11] This ruled out positions 5 and 6, but not positions 1, 4, and 7 as possible sites for phenyl substitution. The 5- and 6-phenyl-2-norbornanones of Sunders and Benjamin[11] were not identical with the starting ketone XIV (Ar = C_6H_5). The NMR spectrum of

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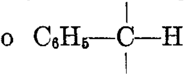
(48) S. Beckmann and R. Schaber, *Ann.*, **585**, 154 (1954).

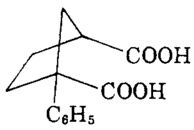
TABLE VIII

PREPARATION OF 1-ARYL-2-ARYL-2-*endo*-NORBORNANOLS, XVI

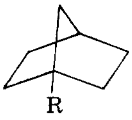
Ar	Ar	Average Yield, %	M.P. B.P.	Empirical Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	X, % Calcd.	X, % Found
C_6H_5	C_6H_5[a]	96.5	109.4–109.8	$C_{19}H_{20}O$	86.32	86.18	7.63	7.39		
C_6H_5	*p*-$CH_3C_6H_4$[a]	61.0	108.4–108.8	$C_{20}H_{22}O$	86.28	86.30	7.97	8.13		
p-$CH_3C_6H_5$[a]	C_6H_5[a]	77.7	121.3–121.7	$C_{20}H_{22}O$	86.28	86.20	7.97	8.14		
p-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$[a]	70.5	118.0–118.4	$C_{21}H_{24}O$	86.25	85.98	8.27	8.24		
									Chlorine	
C_6H_5	*p*-ClC_6H_4[b]	73.6	121.7–122.1	$C_{19}H_{19}OCl$	76.37	76.63	6.41	6.53	11.87	11.37
p-ClC_6H_4	*p*-ClC_6H_4[b]	73.4	$195–205_{0.5}$	$C_{19}H_{18}OCl_2$	68.48	68.70	5.44	5.66	21.28	21.02
									Nitrogen	
C_6H_5	*p*-$N(CH_3)_2C_6H_4$[b]	31.1	122.6–123.2	$C_{21}H_{25}ON$	82.04	81.91	8.20	8.32	4.56	4.70
p-$N(CH_3)_2C_6H_4$	*p*-$N(CH_3)_2C_6H_4$[b]	16.1	147–152 dec.	$C_{23}H_{30}ON_2$	78.81	79.00	8.63	8.79	7.99	8.09
o-$OCH_3C_6H_4$	*o*-$OCH_3C_6H_4$[b]	59.9	149.0–150.7	$C_{21}H_{24}O_3$	77.75	77.53	7.46	7.54		
C_2H_5[c]	C_6H_5[a]	*ca.* 60	83.4–84.4	$C_{15}H_{20}O$	83.28	83.32	9.32	9.44		

[a] Direct addition. [b] *n*-Butyllithium interchange. [c] The preparation of the starting ketone, 1-ethyl-2-norbornanone, will be included in a forthcoming publication.

1-phenyl-norbornane (XXV. R = C_6H_5) confirmed the structure and eliminated the remaining possibility for the hydrocarbon, 7-phenylnorbornene. No  $C_6H_5—\overset{|}{\underset{|}{C}}—H$ proton was detectable in the spectrum. (Hydrogen bonding and solvolysis rate studies also eliminated the 7-phenyl and the 4-phenyl-2-norbornanone structures.)



XXIV

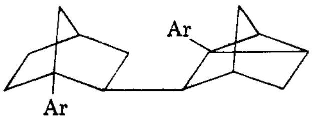


XXV

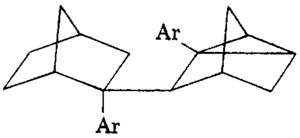
4. There remained the need for a degradation to a substance of known structure to eliminate the unlikely possibility that rearrangement to another ring system had occurred. Wolff-Kishner reduction of 1-*p*-anisyl-2-norbornanone (XIV. Ar = *p*-$CH_3OC_6H_4$) gave 1-*p*-anisylnorbornane (XXV. R = *p*-$CH_3OC_6H_4$). Ozonization[6] gave norbornane-1-carboxylic acid (XXV. R = COOH), identical with an authentic sample.[49] The structure proof is complete.

The structure of the "olefin-dimer" (XI). Solids which gave proper analyses for "olefin-dimer" were isolated as byproducts of the Wagner-Meerwein rearrangements in the phenyl, *p*-tolyl, and *p*-anisyl series. The structures of these materials are not established. The available spectral evidence and the expected mode of formation suggest the possibilities XIA or XIB.

The ultraviolet spectra of the dimers possess no strong absorption bands similar to those of the 2-arylnorbornenes. No evidence for the presence of an olefin could be found in the infrared or NMR spectra. The NMR spectra of the phenyl and anisyl dimers reveal that both are of the same structural type. The two aryl groups in each are in different environments, ruling out a symmetrical, cyclic structure. The phenyl dimer absorbed in the infrared at 751–743 and 698 cm.$^{-1}$, positions characteristic of monosubstituted benzenes.[42] The tolyl and anisyl dimers both had peaks in the 800–823-cm.$^{-1}$ region indicative of *para*-substitution.[42]



XIA



XIB

EXPERIMENTAL

All melting points were taken in soft glass capillaries in a Hershberg apparatus using calibrated thermometers. All boiling points are uncorrected. The NMR spectra were taken with a 40 mc. Varian instrument using carbon tetrachloride solutions and tetramethylsilane as internal standard. The ultraviolet data were obtained using ethanol solutions; infrared spectra were run on pure liquid samples or on carbon disulfide solutions. Microanalyses were carried out by Mr. George Robertson, Florham Park, N. J. Two chlorine analyses were conducted by the Schwartzkopf Microanalytical Laboratory, Woodside, N. J.

2-exo-Norbornyl formate (VA). Approximately 800 g. (17.4 moles) of 98–100% formic acid was added to 400 g. (4.26 moles) of norbornene (IV),[15] and the mixture was refluxed for 4 hr. After removal of excess formic acid, the residue was distilled to give 550 g. (92.5% yield) of 2-*exo*-norbornyl formate (Va), b.p. 65–67° (14–16 mm.), n_D^{25} 1.4597; lit.[17] b.p. 76–77° (20 mm.), n_D^{20} 1.4641.

2-Norbornanone (VI). A solution of 510 g. (3.65 moles) of 2-*exo*-norbornyl formate (Va) and 1.5 l. of A.R. acetone was stirred in 5-l. three necked flask equipped with a thermometer and a dropping funnel containing 8*N* aqueous chromic

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(49)(a) W. P. Whelan, Jr., Ph.D. thesis, Columbia University, 1952; (b) R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958); (c) H. Kwart and G. Null, *J. Am. Chem. Soc.*, **80**, 248, (1958); **81**, 2765 (1959); (d) W. R. Boehme, *J. Am. Chem. Soc.*, **81**, 2762 (1959). We are indebted to Professor H. Kwart for making this comparison.

acid solution.[19] The flask was cooled in an ice bath and the chromic acid was added at a rate so that the reaction temperature was maintained at 20–30°. Approximately 1870 ml. of oxidant solution was required to complete the reaction. The mixture was stirred overnight and the excess chromic acid reduced with sodium bisulfite. The acetone solution was decanted from the precipitated chromic sulfate and washed three times with 200–250 ml. portions of saturated potassium carbonate solution. After drying over anhydrous potassium carbonate, the acetone was distilled; a little benzene was added near the end to assist in the removal of the remaining water by azeotropic distillation. Finally 350 g. (87% yield) of norbornanone was collected, b.p. 170–173°, m.p., crude, 90–91°; lit. b.p. 170.2–170.8°, m.p. 97.2–98.0°[47]; other literature values range from m.p. 90–91° to 95°.[20,47] Gas chromatography revealed the presence of a trace of water, two minor impurities (but no Va or Vb), and a purity of about 96%. The material was sufficiently pure for preparative purposes.

Preparation of 2-aryl-2-endo-norbornanols (VII). *Method A. 2-Phenyl-2-endo-norbornanol.* To an ether solution of phenyllithium prepared from 13.3 g. (1.81 g.-atoms) of lithium and 142.0 g. (1.00 mole) of bromobenzene was added an ether solution of 90.0 g. 2-norbornanone (VI) (0.82 mole) at a rate sufficient to maintain reflux. After stirring for 4 additional hr., the lithium compounds were decomposed with water. The ether layer was separated and the water layer heavily salted and extracted with portions of fresh ether. The combined ether solutions were dried over anhydrous sodium sulfate. The ether and the excess bromobenzene were removed under reduced pressure and the residue was distilled. The yield of crude 2-phenyl-2-*endo*-norbornanol (VII, Ar = C_6H_5) was 73.1% (Table I).

Method B. 2-p-Dimethylaminophenyl-2-endo-norbornanol. To an ether solution of *n*-butyllithium prepared from 15.0 g. (2.06 g.-atoms) of lithium and 114.6 g. (0.91 mole) of *n*-butyl bromide at −15 to −10° was added an ether solution of *p*-bromodimethylaniline (129.5 g., 0.65 mole) during a 15-min. period. An ether solution of 91.5 g. (0.83 mole) of norbornanone was added. The reaction temperature rose during this addition; stirring was continued overnight. After work-up as in Method A and removal of ether solvent under reduced pressure, a mushy solid remained. Crystallization from hot ligroin solution gave 71.1 g. (47.3% yield) of VII (Ar = *p*-$NH_2C_6H_4$), initial m.p. 100.8–102.8°.

The other 2-aryl-2-*endo*-norbornanols VII were prepared in a manner similar to that of Method A, except that aryl Grignard reagents were substituted for the lithium reagent. Physical data and other pertinent information are recorded in Table I. The alcohols were recrystallized from ligroin; *p*-nitrobenzoates[50] from ethanol and the acetate ester[50] of VII (R = C_6H_5) from ethanol-water.

2-Arylnorbornenes (VIII *and* IX). *Method A. Thermal dehydration. 2-p-Anisylnorbornene.* During one preparation of 2-*p*-anisyl-2-*endo*-norbornanol (VII, Ar = *p*-$CH_3OC_6H_4$) distillation during the work-up was carried out at water-pump pressure. The product, an oil which solidified on standing in an ice bath, did not possess OH bands in the infrared. By intentional overheating prior to distillation, solid olefin (2-anisylnorbornene, VIII), b.p. 156–179° (16–20 mm.), was obtained. Recrystallization from ethanol gave a constant m.p. of 44.0–45.2° (reported 44.5–45.8°[6]).

The *p*-tolyl olefin (VIII, Ar = $CH_3C_6H_4$), b.p. 149–157° (14 mm.), n^{20}_{D} 1.57229, was obtained similarly in 57% yield.

Crude 2-*o*-anisylnorbornene (VIII, Ar = *o*-$CH_3OC_6H_4$) (81% yield) was formed by overheating prior to distillation. Redistillation over a few crystals of potassium bisulfate at 2 mm. pressure gave three fractions; b.p. 120–129°, n^{20}_{D} 1.56745; b.p. 130–134°, n^{20}_{D} 1.57223; b.p. 134–135°, n^{20}_{D} 1.57488. The center cut was analyzed.

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.98; H, 7.98.

Method B. Potassium bisulfate dehydration. 2-Phenylbornene. Into a 100-ml. distilling flask was placed 38.0 g. (0.20 mole) of 2-phenyl-2-*endo*-norbornanol (VII Ar = C_6H_5) and 20 g. of potassium bisulfate crystals. The apparatus was arranged for distillation at water-pump pressure. The mixture was warmed gradually, giving first a pink solution, then a yellow oil. The distillate was 26.7 g. (0.17 mole) of a clear colorless oil, b.p. 124–128° at 17 mm., n^{20}_{D} 1.50916. The average yield of three runs was 77.6%.

One gram of 2-phenylnorbornene was added to 2 ml. of freshly distilled phenylazide, but no solid adduct formed after 4 months at room temperature. Characterization of the olefin by derivatization and the establishment of the presence of considerable 1-phenylnortricyclene in the dehydration product will be described separately[25]

The *m*-anisyl olefin VIII (Ar = *m*-$CH_3OC_6H_4$) and the *p*-chlorophenyl olefin VIII (Ar = *p*-ClC_4H_6)[25] were prepared similarly. The ultraviolet data for the principal absorption bands for all these olefins is given in Table II. An infrared bands at 822 cm.$^{-1}$, characteristic of a trisubstituted olefin,[42] is a prominant feature in the spectrum of the phenyl olefin. A band near this position appears in the spectra of the other olefins, but *p*-disubstituted phenyl compounds also absorb in this region[42] so that this feature is inconclusive.

1-Aryl-2-exo-norbornyl formates (Xa). *1-Phenyl-2-exo-norbornyl formate.* To 75 g. of 98–100% formic acid was added 25.0 g. (0.13 mole) of 2-phenyl-2-*endo*-norbornanol and the mixture was heated to 70 ± 2° for 2 hr. on a water bath. Two layers formed immediately and the reaction mixture darkened as time progressed. After the excess formic acid was removed at reduced pressure, the residue was distilled to give 9.2 g. (31.9% yield) of light yellow oil. Oil of the same color and composition was obtained in 30.0% yield when 2-phenylnorbornene (VIII, C = C_6H_5) was used as the starting material. In both preparations the undistilled portion was an extremely viscous yellow-brown oil. Pertinent data on 1-phenyl-2-*exo*-norbornyl formate are recorded in Table III. The other formates in the series (Xa) were prepared in a similar fashion.

1-Aryl-2-exo-norbornyl acetates (Xb). *1-Phenyl-2-exo-norbornyl acetate.* To 113.5 g. (0.60 mole) of 2-phenyl-2-*endo*-norbornanol was added 300 g. of glacial acetic acid and 15 ml. of 50% sulfuric acid; the reaction was maintained at 70 ± 2° for 2 hr. The color of the solution darkened as time progressed. After most of the excess acetic acid was removed at reduced pressure, the residual orange-brown cloudy mixture was poured into water and extracted with ligroin. Sodium carbonate was added during the course of this operation to neutralize the acids present. The combined ligroin extracts were washed with sodium carbonate solution and dried over anhydrous sodium sulfate. After the solvent was removed at reduced pressure, the residue was distilled to give two fractions: 26.9 g. of colorless oil, b.p. 145–156° (13 mm.), n^{20}_{D} 1.5424, and 80.6 g. of colorless oil, b.p. 157–170° (13 mm.). n^{20}_{D} 1.5344. The lower boiling cut was redistilled, its higher boiling cut combined with the first higher boiling fraction, and these redistilled to provide 90.6 g. (65.2% yield) of viscous colorless acetate, b.p. 158–160° (13 mm.), n^{20}_{D} 1.5316. The foreruns from these distillations gave infrared spectra which showed acetate bands, but were quite different in other regions from the spectrum of Xb (R = C_6H_5). No diphenyl could be crystallized from these cuts, nor was an attempt made to determine their composition. A mixture of acetate, diphenyl, and unchanged hydrocarbon (VIII or IX) may have been present.

The acetate Xb (R = C_6H_5) formed a white solid when scratched with a spatula in an ice bath. Pertinent data are recorded in Table III. The other acetates were prepared in a similar fashion. A smaller amount of 50% sulfuric acid was used to catalyze the rearrangements of the 2-*p*-anisyl and 2-*p*-tolyl compounds; a greater amount was used for the 2-

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(50) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, Wiley, New York, Fourth Edition, 1956.

p-chlorophenyl reaction. All the solid esters in Table III, except the *p*-anisyl acetate, were recrystallized from ethanol. Ligroin was used for Xb (Ar = *p*-$CH_3OC_6H_4$).

Dimeric by-product from the rearrangement processes (XI). *2-Phenylnorbornene dimer.* The pot residue left after distillation of the acetate, an extremely viscous yellow-brown oil, afforded some white crystals from ethanol solution, initial m.p. 130–150°, constant m.p. 161.8–162.8°, after three more recrystallizations from ethanol-ethyl acetate.

Anal. Calcd. for $C_{26}H_{28}$: C, 91.71; H, 8.29. Found: C, 91.69; H, 8.30.

The NMR spectrum showed two strong peaks at 2.875 and 3.086 τ for the hydrogens on the two dissimilar phenyl groups. The other hydrogens gave a rather indistinct pattern (see below). The ultraviolet spectrum did not possess an intense band similar to that of 2-phenylnorbornene (VIII R = C_6H_5).

2-p-Anisylnorbornene dimer. During the preparation of 1-*p*-anisyl-2-*exo*-norbornyl acetate (Xb.Ar = *p*-$CH_3OC_6H_4$), a large amount of precipitate formed after about 15 min. of reaction time. This solid was filtered, washed with cold acetic acid, and dried under vacuum. It was identical with material obtained from processing the residue from the distillation of the acetate. Fourfold recrystallization from ethanol–ethyl acetate gave a constant m.p. of 165.2–166.0°. The molecular weight by the Rast method was 335; calcd. for dimer, 400.

Anal. Calcd. for $C_{28}H_{32}O_2$: C, 83.96; H, 8.05. Found: C, 83.71, H, 7.90.

The NMR spectrum showed absorptions at 2.91 and 3.13 τ for the 2 and 2′ aromatic hydrogens, at 3.34 and 3.58 τ for the 3 and 3′ aromatic hydrogens and at 6.322 and 6.402 for the methoxyl hydrogens on the two benzene rings. The values for the aliphatic hydrogens, 7.22, 7.54, 7.86, 8.44, and 8.71 τ probably correspond to the values of 7.15, 7.52, 7.83, 8.44, and 8.74 τ for the aliphatic hydrogens of the 2-phenylnorbornene dimer. The intensity patterns of these peaks are very similar.

2-p-Tolylnorbornene dimer. Crystalline dimer was obtained from the distillation residues of 1-*p*-tolyl-2-*exo*-norbornyl formate and acetate (Xa and Xb, Ar = *p*-$CH_3C_6H_4$) by crystallization from ethanol solution. After four recrystallizations from the same solvent, the material still possessed a wide m.p. range 85–106°.

Anal. Calcd. for $C_{28}H_{32}$: C, 91.25; H, 8.75. Found: C, 91.00; H, 8.83.

1-p-Nitrophenyl-2-exo-norbornyl acetate (XII).[36] A solution of 15.9 g. (0.068 mole) of 1-phenyl-2-*exo*-norbornyl acetate (Xa Ar = C_6H_5), 100 ml. of glacial acetic acid and 100 ml. of acetic anhydride was stirred magnetically. The flask was surrounded by an ice bath. A nitration mixture, prepared by dropping 100 ml. of fuming nitric acid into a stirred ice cold solution of 100 ml. of glacial acetic acid and 100 ml. of acetic anhydride, was added. The temperature of the reaction was maintained below 15°. Stirring was continued for 0.5 hr. after addition of the nitration mixture was complete; the solution was then poured into water. A yellow oil separated and solidified shortly upon standing. The solid was filtered, washed several times with water, and recrystallized from ethanol to give 12.6 g. (66.2% yield) of pale yellow acetate, initial m.p. 97.7–101.5°. The mother liquors gave 3.9 g. of unidentified yellow-orange oil.

Purified 1-*p*-nitrophenyl-2-*exo*-norbornyl acetate (XII) was reduced to the amine Xb (Ar = *p*-$NH_2C_6H_4$) catalytically[37] and reductively dimethylated[38] to the dimethylamine Xb (Ar = *p*-$(CH_3)_2NC_6H_4$). Physical data for these compounds will be found in Table III.

1-Aryl-2-exo-norbornanols (XIII). With the exceptions of the *p*-nitro and amine derivatives, alcohols XIII were prepared by saponification of the corresponding esters X with potassium hydroxide in ethanol solution. Table IV summarizes the observations. The alcohols were recrystallized from liroin. Ethanol was used for the nitro and amine compounds. All *p*-nitrobenzoate derivatives[50] were recrystallized from ethanol.

1-p-Nitrophenyl-2-exo-norbornanol. To a solution of 51.2 g. (0.19 mole) of 1-*p*-nitrophenyl-2-*exo*-norbornyl acetate (XII) in 1.5 l. of acetone was added 75 ml. of concd. aqueous hydrochloric acid and 350 ml. of water. After refluxing the solution for 24 hr., most of the acetone was distilled, and the residual mixture was poured into water. The pale yellow solid which formed immediately was filtered, washed with water and dried to give 37.0 g. (87.5% yield) of alcohol XIII (Ar = *p*-$NO_2C_6H_4$). The amine and dimethylamine derivatives XIII (Ar = *p*-$NH_2C_6H_4$ and *p*$(CH_3)_2NC_6H_4$) were prepared similarly. Amine XIII (Ar = *p*-$NH_2C_6H_4$) was also prepared from XII by the method of Dewar and Mole.[51]

1-p-Nitrophenyl-2-exo-norbornyl nitrate (XVII). The reaction was similar to the nitration of Xb (Ar = C_6H_5) except that the starting material was 5.0 g. (0.027 mole) of 1-phenyl-2-*exo*-norbornanol (XIII Ar = C_6H_5). The solvent was 100 ml. of 1:1 acetic acid–acetic anhydride and about 150 ml. of nitrating reagent was used. The material which precipitated when the reaction mixture was poured into water gave 5.9 g. (96.5% yield) of 1-*p*-nitrophenyl-2-*exo*-norbornyl nitrate (XVII): the m.p. was 68.8–69.4° after three recrystallizations from ethanol.

Anal. Calcd. for $C_{13}H_{14}O_5N_2$: C, 56.11: H, 5.07: N, 10.07. Found: C, 56.38: H, 5.31; N, 10.07.

A blue-green color was formed when a few crystals of the nitrate were added to a solution of diphenylamine in sulfuric acid.[52] The infrared spectrum of the compound had peaks at 1640 and 1275 cm.$^{-1}$, characteristic of covalent nitrate groups.[42]

1-Aryl-2-norbornanones (XIV). *1-Phenyl-2-norbornanone.* The reaction was similar to the preparation of norbornanone (VI). The quantities of materials used were 94.4 g. (0.50 mole) of 1-phenyl-2-*exo*-norbornanol, 350 ml. of A.R. acetone and 175 ml. (125 ml. calcd. amount) of 8*N* chromic acid solution.[19] After separation of chromic sulfate, the acetone solvent was removed under reduced pressure, water was added, the mixture was neutralized with sodium carbonate, and extracted three times with ether. The ether solution was dried over anhydrous sodium sulfate and the solvent evaporated under reduced pressure. Distillation of the residue afforded 52.6 g. (53.6% yield) of light yellow oil, which crystallized to a white solid. The other ketones XIV except Ar = *p*-$NH_2C_6H_4$ and *p*-$(CH_3)_2NC_6H_4$ were prepared in a similar manner. Reduction[37] and reductive alkylation[38] of XIV (Ar = *p*-$NO_2C_6H_4$) gave the amine ketones. XIV (Ar = *p*-$NO_2C_6H_4$) was recrystallized from ethanol, XIV (Ar = *p*-$NH_2C_6H_4$) from ether-ligroin and the remaining ketones from ligroin. The 2,4-dinitrophenylhydrazone derivatives[50] were recrystallized from ethanol. The data are presented in Table V.

Acid by-products from 1-aryl-2-norbornanone oxidations. 1-p-Chlorophenylcyclopentene-3(4)-Acetic acid (XXI, Ar = *p*-ClC_6H_4). The aqueous solution which had been neutralized with sodium carbonate [from the work-up of the oxidation of 1-*p*-chlorophenyl-2-*exo*-norbornanol (XIII, Ar = *p*-ClC_6H_4)] was acidified with dilute sulfuric acid and extracted with ether. The ether solution was dried with anhydrous sodium sulfate and the solvent evaporated. The yellow oil which remained could be crystallized only from ligroin solution with the aid of a Dry Ice–acetone bath. The white crystals had an initial m.p. of 106–112° which was only raised to 107.8–112.8° after seven recrystallizations from ether–petroleum ether (b.p. 30–60°). The neutralization equivalent was 229–231 (calcd. for assumed structure XXI (Ar = *p*-ClC_6H_4), 236.6).

Anal. Calcd. for $C_{13}H_{13}O_2Cl$: C, 65.96; H, 5.54; Cl, 14.98. Found: C, 65.82; H, 5.61; Cl, 14.85.

The ultraviolet data are recorded in Table VI.

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(51) Table IV, footnote b.

(52) H. Wieland, *Ber.*, **46**, 3296 (1913); **52**, 886 (1919); G. W. Manier-Williams, *Analyst*, **56**, 397 (1931).

1-p-Tolylcyclopentene-3(4)-acetic acid (XXI, Ar = *p*-$CH_3C_6H_4$). The acid by-product from the oxidation of 1-*p*-tolyl-2-*exo*-norbornanol (XIII, Ar = *p*-$CH_3C_6H_4$) was obtained as above. White crystals, initial m.p. 106–116°, were recrystallized from ethanol. The melting point after four such operations was 107–118°, the neutralization equivalent was 206–208 [calcd. for structure XXI (Ar = *p*-$CH_3C_6H_4$), 216].

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 75.65; H, 7.44.

The low value for carbon in the above analysis may have been due to the presence of alcohol-acid impurity of the type observed by Mosher and Langerak[46] to be formed during isoborneol oxidation. The ultraviolet spectral data are presented in Table VI.

1-Aryl-2-endo-norbornanols (XV). The reductions of the ketones XIV were carried out with lithium aluminum hydride in the standard manner.[53] A saturated sodium sulfate solution was used to destroy the excess hydride and to decompose the lithium salts. After the ether was removed under reduced pressure, ligroin was added to the residue and crystallization was attempted at reduced temperatures; if crystallization could not be induced, the compound was distilled at reduced pressure.

The reductions with sodium borohydride[54] employed aqueous ethanol as the solvent. A three-fold excess of hydride was employed. After ethanol was removed under reduced pressure, water was added and the product alcohol was extracted with ether. The work-up which followed was as above.

The amino alcohol XV (Ar = *p*-$NH_2C_6H_4$) and the dimethylamino alcohol XV (Ar = *p*-$(CH_3)_2NC_6H_4$) were prepared from nitro alcohol XV (Ar = *p*-$NO_2C_6H_4$) by reductive processes.[37,38] The *p*-nitrobenzoate of the dimethylamino compound was a yellow-orange solid, but gave a pale yellow solution, λ_{max} 257.5 mμ. The λ_{max} of the *p*-nitrobenzoate of 1-ethyl-2-*endo*-norbornanol was at 259 mμ.

The alcohols XV were all recrystallized from ligroin; their *p*-nitrobenzoates from ethanol. Pertinent data appear in Table VII.

1-Aryl-2-aryl-2-endo-norbornanols (XVI). These compounds were prepared by direct addition of an aryllithium reagent to the appropriate 1-aryl-2-norbornanone XIV. The lithium reagents were either prepared directly or by interchange with *n*-butyllithium as outlined above. The methods employed and other data on these compounds are listed in Table VIII. All compounds were recrystallized from ligroin.

Bertram-Walbaum[30] reaction on 1-phenyl-2-phenyl-2-endo-norbornanol (XVI, Ar = Ar′ = C_6H_5). *1-Phenyl-2-phenylnorbornene* (XXII). To a solution of 1.65 g. (6.25 mmoles) of 1-phenyl-2-phenyl-2-*endo*-norbornanol (XVI, Ar = Ar′ = C_6H_5) in 30 ml. of acetic acid was added 1 ml. of 50% sulfuric acid, and heating on the steam bath at a regulated temperature of 70 ± 2° was continued for 2 hr. When the solution was poured into water, a white solid formed immediately. The solid was filtered with suction, washed with water and dried to give 0.95 g. (61.8% yield) of olefin, m.p. 95.4–98.0° after four recrystallizations from ethanol.

Anal. Calcd. for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.43; H, 7.60.

The ultraviolet spectrum in ethanol solution showed λ_{max} 255 mμ, log ϵ 4.10 (compare Table II). The NMR spectrum showed absorptions at 2.828 τ for the 1-phenyl hydrogens (1-phenylnorbornane, 2.849 τ), at 3.097 τ the 2-phenyl hydrogens, at 3.76 τ for the olefinic hydrogen (norbornene, 4.06 τ) and at 6.97 τ for the C-4 bridgehead hydrogen (norbornene, 7.22 τ). The remaining six hydrogens gave an indistinct pattern from 7.8 to 8.7 τ. The spectrum is decisive in rejecting a symmetrical 1,2-diphenylnortricyclene structure, as an olefinic hydrogen and two quite dissimilar phenyls are seen.

Bromination of 1-phenyl-2-phenyl-2-endo-norbornanol (XVI, Ar = Ar′ = C_6H_5). To a solution of 3.5 g. (13 mmoles) of 1-phenyl-2-phenyl-2-*endo*-norbornanol (XVI, Ar = Ar′ = C_6H_5) in 35 ml. of carbon disulfide was added a few crystals of iodine. Approximately 2.2 g. (14 mmoles) of bromine and then 3 drops of pyridine were added dropwise, and stirring was continued for 0.5 hr. The orange-red solution containing a little orange-brown solid was filtered through filteraid and the filtrate evaporated. The light orange solid and orange oil which remained were dissolved in ligroin. Crystallization afforded 2.5 g. (58.3% yield) of white crystals, m.p. 149.7–150.2° after five recrystallizations from ethanol.

Anal. Calcd. for $C_{19}H_{17}Br$: C, 70.16; H, 5.27; Br, 24.57. Found: C, 70.67; H, 5.54; Br, 24.40.

The ultraviolet spectrum in ethanol solution had λ_{max} 253 mμ, log ϵ 4.12. The compound was assigned the structure 1-*p*-bromophenyl-2-phenylnorbornene (XXIII), as the isomeric 2-*p*-bromophenyl compound should give a bathochromically shifted ultraviolet maximum (compare Table II and compound XXII). The infrared spectrum of the compound had a peak at 827 cm.$^{-1}$, attributable to a 1,4-disubstituted benzene,[42] and peaks at 750 and 695 cm.$^{-1}$, characteristic of monosubstituted benzenes.[42]

Friedel-Crafts reaction of acetic anhydride with 1-phenyl-2-exo-norbornyl acetate (Xb, Ar = C_6H_5). *2-Phenyl-3-acetonorbornene* (XVIII). A 500-ml., three necked flask was equipped with a dropping funnel, an electric stirrer, and an efficient reflux condenser topped with a calcium chloride tube. To a solution of 30.8 g. (0.13 mole) of 1-phenyl-2-*exo*-norbornyl acetate (Xb Ar = C_6H_5) in 150 ml. of carbon disulfide was added 55.0 g. (0.41 mole) of anhydrous aluminum chloride. Heat was evolved during the addition and a red-brown solution resulted. The solution was heated on the steam bath until gentle refluxing began; 14.5 g. (0.14 mole) of acetic anhydride was added dropwise. After refluxing for 1 hr., the carbon disulfide was distilled, and the residual red-brown oil was poured into a mixture of cracked ice and hydrochloric acid. Ether was used as the solvent for extraction; the combined extracts were washed with 10% sodium hydroxide solution and with water, and dried over anhydrous sodium sulfate. Distillation of the product gave 14.1 g. (49.6% yield) of yellow oil, b.p. 162–172° at 11 mm., n_D^{20} 1.57159. The ultraviolet spectrum in ethanol had λ_{max} 272, log ϵ 3.83. Infrared bands at 697 and 742 cm.$^{-1}$ indicated a monosubstituted benzene structure.

The 2,4-diphenylhydrazone derivative[50] formed as a brick-red solid, initial decomposition point, 144.4°. After seven recystallizations from ethyl acetate the m.p. was constant, 173.8–174.6°.

Anal. Calcd. for $C_{21}H_{22}N_4O_4$: C, 64.27; H, 5.14; Found C, 64.36; H, 5.14.

The ultraviolet spectrum of this derivative in ethyl acetate showed maxima at 264.5, 288, and 387 mμ with log ϵ 4.13, 3.97, and 4.42 respectively.

Permanganate oxidation of 1-phenyl-2-norbornanone (XIV, Ar = C_6H_5). *1-Phenyl-1,3-cis-cyclopentane dicarboxylic acid* (XXIV) A mixture of 2.0 g. (0.011 mole) of 1-phenyl-2-norbornanone (XIV, Ar = C_6H_5), 3.3 g. (0.021 mole) of potassium permanganate, 0.9 g. of potassium hydroxide and 75 ml. of water was warmed on the steam bath for 0.5 hr. and then filtered with suction. The collected manganese dioxide was washed with water and then with a small amount of ether. The filtrate was concentrated on the steam bath under reduced pressure. The solution was extracted with ether and the extracts dried with sodium sulfate. After the ether had been evaporated, there remained an orange-yellow oil which solidified overnight. Repeated processing gave 210 mg. (8.2% yield) of acid, purified by dissolving it in ether and adding ligroin while evaporating the ether. After four such recrystallizations a constant m.p. 162.4–162.8°, was obtained. The neutralization equivalent

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(53) W. G. Brown, *Org. Reactions*, **Vol. VI**, 469 (1951).

(54) S. W. Chaiken and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 122 (1949).

was 116.5; the calculated value for 1-phenyl-1,3-*cis*-cyclopentanedicarboxylic acid is 117.

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.47; H, 5.99.

1-Phenylnorbornane (XXV. R = C_6H_5). The Huang-Minlon modification[55] of Wolff-Kishner reduction was employed. The quantities of materials used were 14.9 g. (0.08 mole) of 1-phenyl-2-norbornanone (XIV. Ar = C_6H_5), 10 g. of potassium hydroxide, 75 ml. of ethylene glycol and 9 ml. of hydrazine hydrate. The combined distillate and cooled reflux mixture were poured into water, extracted with ligroin and the combined extracts were dried with anhydrous sodium sulfate. After the ligroin was removed at reduced pressure, the residue was distilled to give 12.2 g. (88.3% yield) of very light yellow oil, b.p. 124–128° (16 mm.), n_D^{20} 1.5437.

Anal. Calcd. for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.91; H, 9.34.

The NMR spectrum showed absorptions, in τ units, at 2.849 for the five phenyl hydrogens, at 7.68 for the C-4 bridgehead hydrogen and at 8.383 (shoulder at 8.63) for the remaining ten hydrogens.

1-p-Anisylnorbornane (XXV, R = p-$CH_3OC_6H_4$). The similar reduction of 3.0 g. (0.014 mole) of 1-*p*-anisyl-2-norbornanone (XIV, Ar = p-$CH_3OC_6H_4$) gave 1.8 g. (63.6% yield) of 1-*p*-anisylnorbornane (XXV, R = p-$CH_3OC_6H_4$), b.p. 128–132°. This was oxidized directly (see below).

Norbornane-1-carboxylic acid (XXV, R = COOH). Ozonization of 1.8 g. of 1-*p*-anisylnorbornane (XXV, R = p-$CH_3OC_6H_4$) was carried out in 75 ml. of dichloromethane as described by Bartlett, Webster, Dills, and Richey[6] for the oxidation of *p*-anisylapocyclene to tricyclenic acid. The basic solution obtained during the work-up was extracted with ether to remove neutral material and then acidified with dilute hydrochloric acid. After heavily salting the solution, it was extracted with ether several times. The combined ether extracts were dried over sodium sulfate, the ether evaporated leaving a yellow oil. Sublimation afforded 240 mg. (19.0% yield) of white crystals, m.p. 111.4–112.3°, after three recrystallizations from ligroin (lit. m.p. 111–112,[49d] 112–113,[49c] and 113.8–115.5°[49b]). A direct comparison with an authentic sample of norbornane-1-carboxylic acid proved the identity.[49]

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[CONTRIBUTION FROM THE SINCLAIR RESEARCH LABORATORIES]

Ester Formation in the Hydrogen Fluoride-Catalyzed Reaction of Olefins with Carbon Monoxide

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Esters are produced in fair yield along with acyl fluorides and organic acids by condensation of unbranched olefins with carbon monoxide in the presence of hydrogen fluoride containing small amounts of water. Branched olefins yield only acyl fluorides and acids. Possible mechanisms for the ester formation are discussed.

H. Koch has shown that olefins react rapidly with carbon monoxide at room temperature and moderate pressures in the presence of catalysts such as concentrated sulfuric acid.[1a,1b] anhydrous hydrogen fluoride,[1c] monohydroxyfluoboric acid,[1d] and mixtures of the latter with phosphoric or sulfuric acid.[1d] These reactions are the basis of an elegant synthesis of branched organic acids which are formed by hydrolyzing the reactions products with water. He postulated[1e] the following mechanism:

$$\text{Olefin} + H^+ \longrightarrow R^+$$

$$R^+ + CO \longrightarrow RCO^+$$

$$RCO^+ + HOH \longrightarrow RCOOH + H^+$$

We have confirmed Koch's indication that anhydrous hydrogen fluoride is a powerful catalyst for the olefin–carbon monoxide reaction. However, since the hydrogen fluoride recovered for recycle from the final water–organic acid–catalyst mixture is apt to contain water, the use of "wet" hydrogen fluoride as catalyst[2] was investigated. Our study showed that relatively minor amounts of water in the catalyst affect the course of the reaction and the nature of the products obtained from various types of olefins.

Unbranched olefins (Table I). The reaction of propylene with carbon monoxide in the presence of anhydrous hydrogen fluoride at room temperature resulted in low yields of acyl fluoride and considerable isopropyl fluoride. At a higher temperature, namely 75° (Experiment 1), more acyl fluoride was produced (isolated as acid after hydrolysis) and a slightly smaller amount of isopropyl fluoride. An attempt was made (Experiment 2) to improve the yield of acid from propylene and lessen the amount of isopropyl fluoride by using a catalyst containing water (19.8%). With this catalyst carbon monoxide absorption was negligible until the temperature was

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