maximum ($\epsilon_{291\ m\mu}$ 3,340) and a minimum ($\epsilon_{261\ m\mu}$ 985) in the ultraviolet spectrum.

Anal. Calcd. for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found: C, 85.35; H, 8.03; N, 6.55.

2,4,6-Trimethyl-2'-azidobiphenyl (I).—Amine III (11.07 g., 0.0524 mole) was converted to azide I using procedure B of Smith and Brown[4] with the one modification that 3.72 g. (0.054 mole) of sodium nitrite was used in place of amyl nitrite. The crude azide was extracted from the aqueous reaction mixture with petroleum ether; the extract was concentrated at 40° at reduced pressure and purification of the azide was effected by chromatography on 60 g. of Merck alumina. The yield of pale yellow oil was 11.4 g. (92%) and this material showed strong absorption in the infrared (neat) at 2120 cm.$^{-1}$—the characteristic absorption for the azide group.[16]

Anal. Calcd. for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.80; H, 6.21; N, 81.01.

Pyrolysis of I.—A solution of I (11.4 g., 0.0481 mole) in *n*-hexadecane (10 ml., previously purified by shaking with concentrated sulfuric acid, followed by distillation from sodium) was added dropwise to stirred hexadecane (150 ml.)

(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 230.

maintained at 230° in a nitrogen atmosphere. The decomposition was practically instantaneous, and gas evolution ceased shortly after the final addition, but heating was continued 5–10 min. longer. The cooled solution was chromatographed on a column of 300 g. of Merck alumina. The hexadecane was eluted with petroleum ether, 0.91 g. of crude IV was eluted with 1:3 benzene–petroleum ether; 2.95 g. of crude III followed by 5.9 g. of V were obtained with 1:1 benzene–petroleum ether. A red oil (2 g.) was finally obtained with isopropyl alcohol–benzene. A rechromatograph of each fraction gave the following: 0.45 g. (4.5%) of IV, 2.9 g. (29%) of III and 4.8 g. (48%) of V.

The identity of III was established by m.p., mixed m.p., and infrared (CCl_4) spectrum.

Recrystallization of V from carbon tetrachloride followed by sublimation (100° (0.1 mm.)) gave material of m.p. 149–150° (evac. cap.).

Anal. Calcd. for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 87.02; H, 6.28; N, 6.84.

The carbazole IV, after recrystallization from 95% ethanol and sublimation (100°(1.5 mm.)) had a m.p. of 134°.

Anal. Calcd. for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.85; H, 6.96; N, 6.51.

Carbonium Ions. IX. Monoarylalkyl Cations[1,2]

BY N. C. DENO, PAUL T. GROVES, JOHN J. JARUZELSKI AND MYRON N. LUGASCH

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The electronic absorption spectra and the chemical and thermodynamic stabilities of monoarylalkyl cations have been examined as a function of cation structure.

A series of studies on triarylmethyl cations and diarylalkyl cations[2] led to the development of eq. 1, which relates the position of alcohol–cation (ROH—R^+) equilibria to the concentration of acid in water–strong acid systems. A similar equation, eq. 2, was developed for diarylolefin–diarylalkyl cation (Ol–R^+) equilibria. It was natural to anticipate that these two equations would be applicable to monoarylalkyl cation equillibria; this expectation was tested. For monoarylolefins, it was also necessary to test eq. 3, which although widely applicable to base-protonated base (B–BH^+) equilibria, was not obeyed in the protonation of diarylolefins,[2] and was thus expected to be inapplicable to monoarylolefins.

$$H_R = pK_{R^+} + \log c_{ROH}/c_{R^+} \qquad (1)$$

$$H_R - \log a_{H_2O} = pK'_{R^+} + \log c_{ol}/c_{R^+} \qquad (2)$$

$$H_0 = pK_{BH^+} + \log c_B/c_{BH^+} \qquad (3)$$

A variety of compounds were prepared which are capable of forming monoarylalkyl cations in strong acid, but in no case were the equilibria sufficiently permanent to make precise quantitative measurements. The data in Table I summarize the quantitative data obtained and in general it can be said that monoarylalkyl cations obey the same equations as their triarylmethyl and diarylalkyl cation

congeners. For alcohols that cannot dehydrate to arylolefins, the equilibria are between R^+ and ROH, and eq. 1 is obeyed. For alcohols that can dehydrate to arylolefins, the equilibria are between R^+ and olefin, and eq. 2 is obeyed.

Three basic ideas were utilized in an effort to inhibit the bimolecular destruction reactions (intermolecular self-alkylation, ether formation and hydride transfer) which are usually responsible for the transient nature of monoarylalkyl cation equilibria. The first was to replace hydrogens by methyl groups to form polymethylbenzyl cations of the types I and II. Second was to conjugate the extraordinary stability of the aliphatic bornyl cation with the monoarylalkyl system to form cations of undetermined structure which are isomeric with the 2-arylbornyl cations. These are designated series III. Third was to use cations of type IV which must rearrange through a bridge-head carbonium ion before several of the destruction routes become available. The results for series I–IV will be discussed separately.
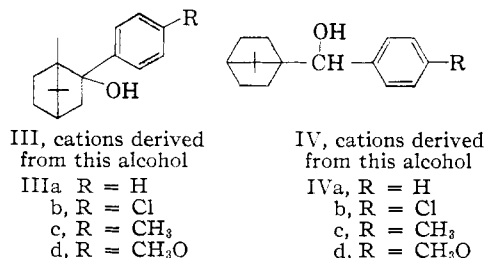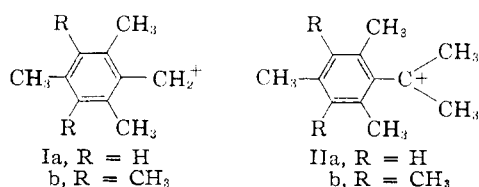
Cations of Type I.—The equilibrium data on cation Ia fit eq. 1 to ±0.1 pK unit from 89–96% H_2SO_4. In the same range, pK calculated by either eq. 2 or 3 continuously changed by 1.2 pK units. A pK calculated on the assumption of an equilibrium between ROH_2^+ and R^+ ($pK = \log a_{H_2O} + \log c_{R^+}/c_{ROH_2^+}$) continuously varied by 1.1 pK units.

These results confirm the interpretation in terms of an ROH–R^+ equilibrium.[3] Further, any olefin

Ia, R = H
b, R = CH₃

IIa, R = H
b, R = CH₃

III, cations derived
from this alcohol
IIIa R = H
b, R = Cl
c, R = CH₃
d, R = CH₃O

IV, cations derived
from this alcohol
IVa, R = H
b, R = Cl
c, R = CH₃
d, R = CH₃O

in equilibrium with R⁺ would have to be of the quinonedimethane type which are known to be unstable.[4]

Attempts to recover 2,4,6-trimethylbenzyl alcohol from 10^{-2} molar solutions of Ia in 97% sulfuric acid gave oils showing no OH band in the infrared spectrum. It seems preferable at present to interpret such a failure to recover the alcohol as due to the incursion of bimolecular destruction reactions, whose rate would be 10^6 faster in the 10^{-2} molar solutions relative to the 10^{-5} molar solutions used in the spectra studies.

In contrast to Ia, cation Ib was unstable even in 10^{-5} molar solution in 97% sulfuric acid. The intense absorption at 480 mμ faded and was replaced by a maximum at 395 mμ characteristic of protonated hexamethylbenzene.[2] This interpretation was verified by adding 2,3,4,5,6-pentamethylbenzyl alcohol to 97% acid to produce a 10^{-2} molar solution of Ib. After 10 min., the solution was drowned in water producing an 80% yield of hexamethylbenzene (VI) calculated on the basis of eq. 4. This appears to be the first example of disproportionation of a monoarylalkanol through hydride transfer, although this reaction is well-known in the diarylalkanol series.[5]

$$\text{(4)}$$
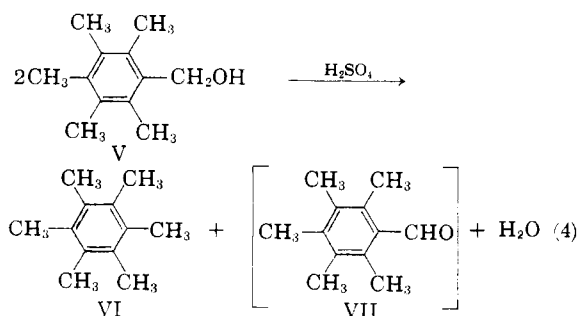
The other product was presumably pentamethylbenzaldehyde (VII) or a tautomer since the hydride may be lost by a CH₃ group. The aldehyde VII would lose CO, forming pentamethylbenzene,[6]

(4) L. A. Auspos, L. A. Hall, J. K. Hubbard, W. Kirk, Jr., J. R. Schaefgen and S. B. Speck, J. Polymer Sci., 15, 9 (1955); M. Levy, M. Szwarc and J. Throssell, J. Chem. Phys., 22, 1904 (1954).

(5) P. D. Bartlett and J. D. McCollum, This Journal, 78, 1441 (1956).

(6) W. M. Schubert and H. Burkett, ibid., 78, 64 (1956); W. M. Schubert and P. C. Myhre, ibid., 80, 1755 (1958).

which would sulfonate thus accounting for VI being the only ether-extractable product.

Cations of Type II.—The data approximately fit either eq. 1 or 2. In both cases the pK values continuously varied by about 0.4 pK unit over the region studied. Although the data do not distinguish between eq. 1 and 2, the fact that the alcohol derived from IIa readily dehydrates to the olefin in dilute acids[7] is evidence that the equilibrium is tween R⁺ and olefin. The pK values in Table I were thus calculated on the basis of eq. 2 for both IIa and IIb.

Cations of Type III.—The data generally fit eq. 2 best suggesting that the equilibria are between R⁺ and olefin. The isolation of monomeric hydrocarbon from IIIa supports this view. The extrapolation of the data to zero time was hindered by the fact that the cation did not instantly form (half-life of formation of IIIa at 25° was about 40 sec.) which decreased the precision of the data.

Although the structures of series III cations are unknown, all four cations appear to possess the same type of structure because the effect of p-substituents on the pK and spectra are similar to that found in the diarylalkyl and triarylmethyl series. A plot of σ^+ for the substituent[8] vs. pK'_{R^+} is linear and the value of ρ is -4.0. The value of ρ per phenyl ring is also about -4.0 for the ROH–R⁺ equilibria in the diarylmethyl[2] and triarylmethyl[3] cation series.

The rate of disappearance of IIIa in 65% sulfuric acid was a second-order process which rendered recovery experiments difficult. However, the great stability of 10^{-5} molar solutions of IIIa in 97% acid encouraged the examination of material formed by drowning 10^{-2} molar solutions of IIIa in 97% acid. Such an experiment gave an 80% yield of liquid C₁₆H₂₀ hydrocarbons, b.p. 86–90° (10 mm.), which were not absorbed from benzene solution by chromatography on alumina. The carbon–hydrogen analyses were complicated by the rapid absorption of oxygen (?) so that the sum of % C and % H was 96% when analyzed and dropped to 94% and 91% on successive days. However, the ratio C₁₆-H₂₀ was precisely preserved.

Gas chromatography showed the presence of three components in the approximate percentages 65, 6 and 29% with the relative retention times of 32.1, 40.7 and 45.0 min. ($T = 205°$, Apiezon absorbent). The two major components cannot be α-phenylcamphene because the prominent absorption at 11.33 μ and lesser peaks at 8.75, 8.80 and 9.05 μ, all characteristic of α-phenylcamphene, are absent in the infrared spectrum of the recovered C₁₆H₂₀ mixture. This conclusion was supported by the ultraviolet absorption spectrum. The above C₁₆H₂₀ mixture had an absorption maximum at 288 mμ in contrast to α-phenylcamphene which has a maximum at 250 mμ. Further, IIIa was formed from α-phenylcamphene and from 2-phenylborneol at the same first-order rate suggesting that they formed IIIa via a common intermediate.

The above results show that IIIa is in equilibrium with hydrocarbons other than α-phenylcamphene despite the fact that α-phenylcamphene

(7) M. S. Newman and N. Deno, ibid., 73, 3644 (1951).

(8) N. Deno and W. L. Evans, ibid., 79, 5804 (1957).

is produced in 60% yield by heating 2-phenylbor-neol with 50% sulfuric acid at 80°.[9] The absorption maximum at 288 mμ suggests that the $C_{16}H_{20}$ mixture formed from IIIa contains phenylcyclopropanes or conjugated phenylolefins. The ratio 65/29 found for the two major components is reminiscent of the ratio 77/23 found for the equilibrium between nortricyclene and norbornene.[10]

A simple monoarylalkyl cation structure for the ions of series III does not account for their unusual thermodynamic stability relative to other monoarylalkyl cations. A similar problem arises in the cation obtained by treating either VIII or IX with acid.[11] This cation is comparable in stability to IIId, being half formed in about 50% sulfuric acid.[12] The stability of a third unusually stable monoarylalkyl cation, X, was explained on the basis of favorably placed π-bonding.[13] Such an explanation cannot apply to ions of series III or the ion from VIII unless the bicyclic system opened to a monocyclic system generating a double bond.

VIII

IX

cis form
X
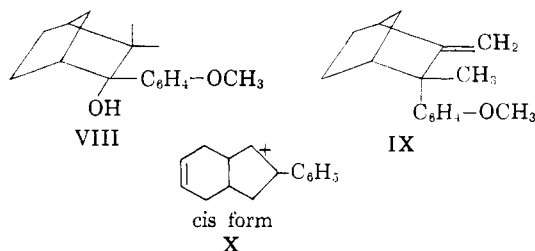
Cations of Type IV.—These were chemically unstable as shown by the data in Table II. Semi-quantitative data were obtained for IVa which fit eq. 2 suggesting that rearrangement had taken place forming an arylolefin which equilibrated with the cation. There is even some question whether a monoarylalkyl cation was present since the absorption maxima for series IV ranged from 330–350 mμ, which is lower than for the other monoaryl-alkyl cations studied. The effect of the substituent on the stability of the ion, as judged by the % acid where the colored species was half formed, was similar to other series of arylalkyl cations.

Other Monoarylalkyl Cations.—The monoaryl-alkyl cations other than those of series I–IV were unstable so that only qualitative data were obtained and these data are summarized in Table II. The electronic absorption spectra for the benzyl cation in 100% sulfuric acid has been reported.[14] The λ_{max} 470 mμ and log ϵ 3.5 are in agreement with predictions from LCAO MO theory.[2] The absorption spectra for the α-methyl and α,α-dimethyl-benzyl cations were also reported,[14] but these spectra may actually be those of the dimer. The absorption of monomeric and dimeric ions would be similar so that the published values[14] can at least stand as estimates.

(9) S. S. Nametkin, H. S. Kichkina and D. N. Kursanov, *J. Russ. Phys.-Chem. Soc.*, **61**, 1065 (1929); *C. A.*, **24**, 841 (1930); H. Rupe and A. Wirz, *Verhandl. Naturforsch. Ges. Basel*, **38**, 164 (1927); *C. A.*, **23**, 1406 (1929).

(10) P. von R. Schleyer, THIS JOURNAL, **80**, 1700 (1958).

(11) P. D. Bartlett, E. R. Webster, C. E. Dills and H. G. Richey, Jr., *Ann.*, **623**, 217 (1959).

(12) P. D. Bartlett and F. T. Wallenberger, private communication.

(13) G. Leal and K. Petit, THIS JOURNAL, **81**, 3160 (1959).

TABLE I

SPECTRA AND STABILITY OF MONOARYLALKYL CATIONS

Cation[a]	λ_{max}, mμ	log ϵ	% H_2SO_4 half ionized[b]	pK[c]	Eq. used to calc. pK
Ia	470	3.47	92.5	−17.3	1
IIa	360	4.25	84.0	−12.2	2
IIb	380	4.02	85.6	−12.4	2
IIIa	415	4.70	62.7	− 8.8	2
IIIb	431	4.93	66.2	− 9.4	2
IIIc	432	4.79	60.8	− 8.4	2
(IIId)[d]	460	3.6	50.3	− 6.4	2
	388	4.64			
IVa	328	3.72	82	−12.0	2

[a] Structures given in text. [b] The % H_2SO_4 where concn. of cation equals concn. of alcohol or olefin. [c] The quantitative data are presented in detail in the Ph. D. Thesis of Paul T. Groves, Pennsylvania State Univ., 1959. The equilibria were studied over a 100-fold change in the ratio R^+/ROH or Ol. The average deviation in pK was generally 0.1. [d] The value of log ϵ at 388 mμ decreased from 4.75 at 60% H_2SO_4 to 4.64 in 97% acid, although the position of the maximum remained constant at 388 mμ. This change may be due to partial protonation of the methoxy group in 97% acid.

Experimental

Most of the compounds employed in this study have been used in earlier papers in this series or are well-known. The 2,3,4,5,6-pentamethylbenzyl alcohol was synthesized by a new method to verify its identity. All of the other compounds whose synthesis are reported below do not appear to have been previously prepared.

2,3,4,5,6-Pentamethylbenzyl alcohol (XI) had previously been prepared by reducing pentamethylbenzoyl chloride with LiAlH$_4$.[8] The product melted at 160° although a m.p. of 137° had also been reported.[15] Alcohol XI has now been prepared by a new method which gave samples identical in m.p. and infrared spectrum with our original sample. It now seems conclusive that the m.p. of XI is 160°.

Pentamethylbenzene was chloromethylated by the method of Vavon and Bolle,[16] which involved heating 13.5 g. of pentamethylbenzene, 9 g. of chloromethyl ether and 100 ml. of acetic acid at 100° for 17 hr. The mixture was poured onto water which precipitated 17 g., m.p. 161–165°, of white crystals of pentamethylbenzyl chloride. This was not further purified, but was hydrolyzed by refluxing in 150 ml. of 1:1 water–dioxane containing 0.3 g. of sodium hydroxide.

The initial product after crystallization from alkanes was a mixture of prisms and needles and melted at 133–135°, reminiscent of the m.p. reported by Clement.[15] A solution of the mixture in 1:1 benzene–hexane was chromatographed on alumina. A small amount of white crystals, m.p. 169–171°, passed through and was not further investigated. Elution with ether containing 2% ethanol gave 2.8 g. of XI in an over-all yield of 18% from pentamethylbenzene.

7,7-Dimethylbicyclo [2.2.1]heptanecarbonyl Chloride (XII).—Commercially available *dl*-10-camphorsulfonic acid was converted to the acid chloride with an excess of thionyl chloride. The yield of *dl*-10-camphorsulfonyl chloride after recrystallization from alkanes was 90%, m.p. 80–82°.[17]

The sulfonyl chloride was oxidized to ketopinic acid with alkaline permanganate as previously described.[18] When the amount of sulfonyl chloride oxidized was 30 g., the yield of ketopinic acid varied between 14 and 30%. Attempts to conduct the oxidation on a larger scale resulted in lower yields. Oxidation of the free sulfonic acid gave only a 3% yield and oxidation of the sulfonamide failed to yield any ketopinic acid.

(14) J. A. Grace and M. C. Symons, *J. Chem. Soc.*, 958 (1959).

(15) H. Clement, *Ann. chim.*, **13**, 243 (1940).

(16) G. Vavon and J. Bolle, *Compt. rend.*, **204**, 1826 (1937).

(17) J. Read and R. A. Storey, *J. Chem. Soc.*, 2768 (1930).

(18) P. D. Bartlett and L. H. Knox, THIS JOURNAL, **61**, 3184 (1939).

TABLE II

% H₂SO₄ AT WHICH MONOARYLALKANOL AND/OR MONOARYLOLEFIN IS HALF CONVERTED TO MONOARYLALKYL CATION

Monoarylalkanol or monoarylolefin added	λmax, mμ and (log ε) or color	% H₂SO₄ where half-ionized	Approximate half-life of cation (sec.) at 10⁻⁵ M	
			% H₂SO₄ in prev. column	97% H₂SO₄
Benzyl alcohol	Orange-red	97		<1
2,4,6-Trimethylbenzyl alcohol	470 3.47	92.5	>60	>60
2,3,4,5,6-Pentamethylbenzyl alcohol	480 3.91	80	1	>60
α-Methylstyrene^a	Yellow	91	(>60)	(>60)
α,4-Dimethylstyrene^a	Yellow	87	(>60)	(>60)
α,2,4,6-Tetramethylstyrene	360 4.25	84.0	360	1000
α,2,3,4,5,6-Hexamethylstyrene	380 4.02	85.6	>1000	1000
4-Fluoro-α-methylstyrene^a	Yellow^b	88	b	(>60)
4-Chloro-α-methylstyrene^a	Yellow	92	(15)	(>60)
4-Methoxy-α-methylstyrene^a	Yellow	62	1	>60
3-Chloro-α-methylstyrene		>97		
4-Isopropenylbenzoic acid		>97		
4-Nitro-α-methylstyrene	Orange-red	95^g	3	3
1-Methylindene^c	400 3.06	78	>60	>60
1-Methyl-3,4-dihydronaphthalene^c	430 2.81			
α-Alkylbenzyl alcohol^d	328 3.72	82	>60	>60
4-Chloro-α-alkylbenzyl alcohol^d	350 3.92	81	60^e	>60^e
4-Methyl-α-alkylbenzyl alcohol^d	332 4.02	77	5^f	>60^f
4-Methoxy-α-alkylbenzyl alcohol^d	352 4.01	64	5^f	>60^f
α,α-Dicyclohexylbenzyl alcohol	Yellow	88	>60	>60

[a] These olefins immediately dimerize in the acid concentrations used so that the monoarylalkyl cations were actually those derived from the dimeric olefin. In the case of α-methylstyrene, it was demonstrated that the dimer (2,4-diphenyl-4-methyl-2-pentene) gave the same results as monomeric α-methylstyrene. The structure of the dimeric olefin is such that it would half-protonate at nearly the same acid concentration as the monomer. Thus the values in column 3 are good estimates for the monomeric olefins. However, the approximate half-lives (columns 4 and 5) refer only to the cation of the dimeric olefin. [b] The yellow color was rapidly replaced by a cloudy pink color. [c] This may be dimeric olefin similar to the situation explained in footnote a. [d] The alkyl group is 7,7-dimethylbicyclo[2,2,1]heptyl. [e] The yellow color formed on fading of the orange color was permanent. [f] The initial pink color faded to yellow within 2 sec. The estimates of the % H₂SO₄ where half-ionized (column 3) were based on this initial pink color. The times listed in columns 4 and 5 refer to the subsequent fading of the yellow color. [g] A pale but relatively permanent yellow color (half formed in 84% acid) is thought to be due to an impurity.

The reduction of ketopinic acid to 7,7-dimethylbicyclo-[2,2,1]heptanecarboxylic acid (XIII) by the Clemmensen method in 60% yield has been reported.[18] It was found that reduction by the hydrazine method[19] gave an 87% yield. The reduction was carried out by mixing a solution of 70 g. of ketopinic acid in 500 ml. of ethylene glycol with a solution of 50 g. of sodium hydroxide, 75 g. of hydrazine and 50 g. of water. The mixture was refluxed for 90 min. after which the temperature was raised to 205–210° by distilling off water and hydrazine. After heating for 5 hr. at 210°, the acidic fraction was isolated by conventional procedures and the acid, m.p. 215–217°, was crystallized from ethanol-water.

The acid XIII was converted to the acid chloride XII by refluxing for 1 hr. with an excess of thionyl chloride containing a trace of pyridine. The yield of XII after crystallization from benzene was 90%, m.p. 83–85°. This product was used in the subsequent syntheses without further purification. The identity of XII was supported by the neut. equiv.: calcd. 93.3, found 94.0.

Phenyl 7,7-Dimethylbicyclo[2,2,1]heptyl Ketone (XIV).—A solution of 36 g. of XII in 75 ml. of benzene was added over 15 min. to a stirred suspension of 27 g. of aluminum chloride in 125 ml. of benzene. After 3 hr. at 25°, the mixture was hydrolyzed and ether extracted. The ether solution was washed with water and steam distilled. The ether extract of the residue was washed with 5% sodium hydroxide (10 g. of XIII was recovered), dried and distilled. The 6.5 g. (22%) of distilled XIV, b.p. 110–120°(0.5 mm.), solidified, m.p. 48–49°. Recrystallization from ethanol raised the m.p. to 49–50°.

Anal. Calcd. for C₁₆H₂₀O: C, 84.16; H, 8.82. Found: C, 84.40; H, 9.05.

The 2,4-dinitrophenylhydrazone was prepared, m.p. 194–195° after recrystallizations from ethanol.

Anal. Calcd. for C₂₂H₂₃O₄N₄: C, 64.85; H, 5.69. Found: C, 64.59; H, 5.81.

(19) Huang-Minlon, This Journal, 68, 2487 (1946).

α-Phenyl - 7,7 - dimethylbicyclo[2,2,1]heptanemethanol (XV).—The ketone XIV was reduced by LiAlH₄ in ether to give an 84% yield, m.p. 100–102°, of white cubes of XV. Recrystallization from alkanes raised the m.p. to 102.5–103.5°.

Anal. Calcd. for C₁₆H₂₂O: C, 83.42; H, 9.63. Found: C, 83.61; H, 9.72.

4-Methoxyphenyl 7,7-Dimethylbicyclo[2,2,1]heptyl Ketone (XVI).—A solution of 10 g. of the acid chloride XII in 20 ml. of anisole was added with stirring to a suspension of 15 g. of aluminum chloride in 50 ml. of carbon disulfide. After standing 1 day, the mixture was hydrolyzed, ether extracted, and the ether extract washed with 5% sodium hydroxide. Steam distillation of the ether solution left a residue which could be crystallized from ethanol to give 10.3 g. (74%) of ketone XVI, m.p. 77–79°. The highest m.p. obtained was 78–79.5°.

Anal. Calcd. for C₁₇H₂₂O₂: C, 79.03; H, 8.58. Found: C, 78.66; H, 8.72.

The 2,4-dinitrophenylhydrazone melted at 155.5–157° after recrystallizations from ethanol.

Anal. Calcd. for C₂₃H₂₅O₅N₄: C, 63.14; H, 5.76. Found: C, 63.13; H, 6.04.

α-(4'-Methoxyphenyl)-7,7-dimethylbicyclo[2,2,1]heptanemethanol(XVII) was reduced with LiAlH₄ in ether to give a 92% yield of white crystals of XVII, m.p. 59–61°. The highest m.p. obtained by recrystallizations from alkanes was 60–62°.

Anal. Calcd. for C₁₇H₂₄O₂: C, 78.41; H, 9.29. Found: C, 78.17; H, 9.48.

4-Methylphenyl 7,7-dimethylbicyclo[2,2,1]heptyl ketone (XVIII) was synthesized by two independent methods. In the first method, a solution of 4-methylphenylmagnesium bromide (prepared from 0.06 mole of 4-bromotoluene) was added to an ether solution of 0.06 mole of the acid chloride XII. The ketone was isolated by conventional pro-

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MONOARYL CATIONS

cedures in 47% yield. The highest m.p. obtained by recrystallizations from ethanol was 64.5–65.5°.

In the second method, a solution of 20 g. of the same acid chloride XII in 50 ml. of toluene was added to a stirred suspension of 30 g. of aluminum chloride in 80 ml. of toluene. The ketone was isolated in the same way as the ketone XVI. The total weight of residue from the steam distillation was 13 g., but only 4.2 g. (16%) of pure XVIII could be obtained by crystallization from ethanol.

Anal. Calcd. for $C_{17}H_{22}O$: C, 84.24; H, 9.14. Found: C, 83.97; H, 9.31.

The 2,4-dinitrophenylhydrazone melted at 154–155.5° after crystallization from ethanol–ethyl acetate.

Anal. Calcd. for $C_{23}H_{25}O_4N_4$: C, 65.54; H, 5.98. Found: C, 65.57; H, 6.17.

α-(4'-Methylphenyl)-7,7-dimethylbicyclo[2,2,1]heptane-methanol (XIX).—The ketone XVIII was reduced with LiAlH₄ in ether to give an 89% yield of white crystals of XIX, m.p. 73–75°. The highest m.p. obtained by recrystallizations from alkanes was 76–77.5°.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.38; H, 9.89. Found: C, 83.78; H, 9.99.

4-Chlorophenyl 7,7-dimethylbicyclo[2,2,1]heptyl ketone (XX) was prepared in 67% yield, m.p. 104–105.5°, by the reaction of 4-chlorophenylmagnesium bromide with the acid chloride XII analogous to the synthesis of the ketone XVIII. The highest m.p. obtained for XX by recrystallization from ethanol was 108–109°.

Anal. Calcd. for $C_{16}H_{19}OCl$: C, 73.12; H, 7.29. Found: C, 73.76; H, 7.38.

The 2,4-dinitrophenylhydrazone melted at 209–210.5°.

Anal. Calcd. for $C_{22}H_{22}O_4N_4Cl$: C, 59.79; H, 5.02. Found: C, 59.78; H, 5.19.

A 30% yield of crude ketone XX was obtained by refluxing the acid chloride XII with aluminum chloride in excess chlorobenzene. The product could not be crystallized. It was identified and the % yield computed by conversion to the 2,4-dinitrophenylhydrazone.

α-(4'-Chlorophenyl)-7,7-dimethylbicyclo[2,2,1]heptane-methanol (XXI).—The ketone XX was reduced with LiAlH₄ in ether to give a 92% yield of the alcohol XXI, m.p. 67–68°. The highest m.p. obtained by recrystallizations from alkanes was 69–70°.

Anal. Calcd. for $C_{16}H_{21}OCl$: C, 72.57; H, 7.99; Cl, 13.39. Found: C, 72.62; H, 8.07; Cl, 12.94.

7,7-Dimethylbicyclo[2,2,1]heptanecarboxylic Anhydride.—An attempt was made to acylate N,N-dimethylaniline with the acid XIII by refluxing a dimethylaniline solution of the acid with phosphorus pentoxide supported on Hyflosupercel. This method of acylation has been successful with other acids.[20] However, in this case, the principal product (40% yield) was the anhydride of the acid XIII. This anhydride can be recrystallized as white prisms from boiling ethanol, m.p. 127–129°. Despite this surprising stability to ethanolysis, its identity as the anhydride seems assured by its analysis and by its reduction to 7,7-dimethylbicyclo[2,2,1]heptanemethanol in 87% yield using LiAlH₄ in ether.

Anal. Calcd. for $C_{20}H_{30}O_3$: C, 75.47; H, 9.71. Found: C, 75.77; H, 9.43.

The 7,7-dimethylbicyclo[2,2,1]heptanemethanol, m.p. 197–199°,[21] was also prepared in 80% yield by reduction of the free acid XIII by LiAlH₄ in ether.

Bis-(7,7-dimethylbicyclo[2,2,1]heptyl)ethan-2-ol-1-one (XXII).—Methyl 7,7-dimethylbicyclo[2,2,1]heptanecarboxylate (the methyl ester of acid XIII) was prepared by adding the acid chloride XII to methanol. The yield of colorless ester was 88%, b.p. 68–74%/(4 mm.) The ester was not further purified or analyzed but applied directly to the following acyloin reaction.

A colloidal suspension of 2.6 g. of sodium in 250 ml. of toluene under dry nitrogen was prepared using a Premier Mill Co. dispersator. To the refluxing suspension was added a solution of 10 g. of the above ester in 25 ml. of toluene. After refluxing for 10 hr., the mixture was cooled

and neutralized with 7 ml. of acetic acid added to the vigorously stirred suspension. The sodium acetate was removed by filtration and the toluene removed by distillation at 10 mm. The residue was dissolved in pentane, water washed, and dried. Evaporation of part of the pentane gave 5.9 g. (70%) of white needles, m.p. 102–108°. Recrystallization from alkanes raised the m.p. to 126.5–127.5°. The product appears to be the acyloin XXII as evidenced by the analysis and the fact that the mixed m.p. experiments showed that the product was not the acid XIII or its corresponding alcohol. The infrared absorption spectrum had bands indicating the presence of hydroxyl and carbonyl groups.

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.59. Found: C, 79.05; H, 10.51.

1,7,7-Trimethyl-2-(4'-methoxyphenyl)-bicyclo[2,2,1]-2-heptanol (XXIII) and 1,7,7-Trimethyl-2-(4'-methoxyphenyl)-bicyclo[2,2,1]-2-heptene (XXIV).—A solution of 38 g. of dl-camphor in 75 ml. of ether was added to the Grignard reagent prepared from 66 g. of 4-bromoanisole in 500 ml. of ether. After stirring for 1 day, saturated ammonium chloride solution was added. The ether layer was washed with 5% potassium hydroxide, dried, and distilled. The distillate, 10.95 g., b.p. 205–206°(15 mm.), quickly solidified, m.p. 65–86°. Recrystallizations from 10:1 pentane–benzene ultimately gave 0.3 g. of white prisms of the alcohol XXIII, m.p. 98.5–101°. The identity was indicated by the analysis and the presence of strong absorption at 2.81 μ which is indicative of a hydroxyl group.

Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.46; H, 9.23. Found: C, 78.56; H, 9.15.

During the 5% potassium hydroxide washings, a semi-crystalline mass collected at the alkali–ether interface. This was collected and steam distilled and the residue from the steam distillation was ether extracted, dried, and distilled. The distillate, 6.5 g., b.p. 182–186° (15 mm.), quickly solidified, m.p. 65–69.5°. Recrystallizations from methanol ultimately gave 0.40 g. of white prisms, m.p. 67–69°. The b.p. analysis, absence of absorption in the 2.8μ region (indicating absence of a hydroxyl group), and the fact that it decolorizes bromine in carbon tetrachloride are all compatible with structure XXIV or an isomer.

Anal. Calcd. for $C_{17}H_{22}O$: C, 83.89; H, 9.11. Found: C, 84.29; H, 9.09.

The total yield of XXIII and XXIV was 17 g. (26%) which is comparable to the yield of the alcohol obtained by treating camphor with phenylmagnesium bromide. The m.p. of 85° for XXIV[22] was not substantiated.

1,7,7-Trimethyl-2-(4'-methylphenyl)-bicyclo[2,2,1]-2-heptanol (XXV).—A solution of 38 g. of camphor in 75 ml. of ether was added to the Grignard reagent prepared from 56 g. of 4-bromotoluene in 500 ml. of ether. The product was isolated as in the case of XXIII to yield 18 g. (29%) of distillate, b.p. 179–181° (13 mm.), which quickly solidified, m.p. 45–78°. Recrystallization from pentane ultimately gave 0.5 g. of white prisms of XXV, m.p. 86.5–89°. The presence of the OH group was indicated by strong absorption at 2.80 μ. Leduc[22] obtained XXV as an oil.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.60; H, 9.84. Found: C, 83.61; H, 10.78.

1,7,7-Trimethyl-2-(2'-methylphenyl)bicyclo[2,2,1]-2-heptanol was made in a manner identical with XXV except that 2-bromotoluene was used. The distillate, b.p. 181–182°(13 mm.), was obtained in 6% yield and failed to crystallize.

Anal. Calcd. for $C_{17}H_{24}O$: C, 83.60; H, 9.84. Found: C, 83.08; H, 10.14.

1,7,7-Trimethyl-2-(4'-chlorophenyl)-bicyclo[2,2,1]-2-heptanol was made in a manner identical with XXV except that 4-bromochlorobenzene was used. The distillate, b.p. 206–208°(15 mm.), solidified, m.p. 50–61°, and was obtained in 29% yield. Recrystallization from pentane gave a 15% yield, m.p. 64–68°. The presence of the OH group was indicated by the strong absorption at 2.80 μ.

Anal. Calcd. for $C_{16}H_{21}OCl$: C, 72.59; H, 7.94. Found: C, 72.77; H, 7.99.

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(22) S. Leduc, *Compt. rend.*, **180**, 1502 (1925).