Acid-catalyzed Isomerization of Substituted Indenes: Attempted Synthesis of Indenylacetone from Prop-2-ynylindene

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Hydration of 3-prop-2-ynylindene gave a substantial quantity of 1-acetonylideneindane (III). The isomerization of the double bond from the five-membered ring of indene to the *exo*-position is explained in terms of an equilibrium between acetonylindene (II) and 1-acetonylideneindane (III): this isomerization was catalyzed by acids. A similar equilibrium was found in the acid-catalyzed isomerization of 3-benzylindenes $C_9H_7{\cdot}CH_2Ph \rightleftharpoons C_9H_8{=}CHPh$.

Both steric and conformational effects were shown to influence this equilibrium very strongly.

ACETYLENIC groups are known to undergo hydration with sulphuric acid and mercuric ions as catalyst to give ketones.[1] With 3-prop-2-ynylindene (Ia) this reaction gave a liquid mixture from which 1-acetonylideneindane (III), m.p. 56°, was isolated (25%). The i.r. spectrum showed strong bands at 5·95 (unsatd. C=O), 6·25 (C=C), and 13·3 μ (benzene ring) and was very different from that of (Ia), which showed absorption at 6·17, 12·9, and 13·95 μ (and acetylenic absorption at 3·05 and 4·7 μ) which were also observed in the spectrum of indene (6·2, 13·03, and 13·95 μ) and 3-benzylindenes (*ca.* 6·2, 12·95—13·0, and 13·95 μ).

TABLE 1

U.v. spectra

$\lambda_{max.}$ (ε): indene 248 (9460); prop-2-ynylindene (Ia) 252 (8400), cinnamaldehyde (2) 343 (25,000), 1-acetonylideneindane 317 (14,000), and 294 (11,800), 3-benzylindene (V) 250 (10,500), 1-benzylideneindane (VI), 330 (22,500), 316 (30,000), 305s (22,700), 296 (22,700), 284 (21,600), 228 (13,500), and 205 (25,000), *trans*-stilbene * 307 (28,000), 295 (29,000), and 228 (12,800), *cis*-stilbene * 280 (25,200) and 224 (27,500).

* G. Berti and Bottari, *Gazzetta*, 1959, **89**, 2371.

The u.v. spectrum was also very different from that of prop-2-ynylindene and closely resembled that of cinnamaldehyde [2] (see Table 1).

The n.m.r. spectroscopic data for the ketone (III) confirmed the structure: τ 3·3 (1H, olefinic), 6·8 (complex, 4H, CH_2) and 7·73 (3H, Me). For the isomeric structure (II) two well separated signals of the CH_2 protons were to be expected (*cf.* n.m.r. spectra of benzylindene and benzylideneindane described below).

Attempts to isolate the second isomeric ketone (II) from the reaction mixture failed although its presence in equilibrium with the ketone (III) under the acidic conditions of the hydration reaction was indicated by strong carbonyl absorption in the i.r. region at 5·83 μ. When the pure ketone (III) was isomerized in ethanol–water (3 : 1) in the presence of 1% sulphuric acid the i.r. spectrum showed that an identical equilibrium mixture was obtained after 15 min.; the amount of (III) was *ca.* 55—60% (as shown by u.v. spectroscopy).

No bond migration occurred in (Ia) before hydration. Under the described acidic conditions, but in the absence of mercuric sulphate, hydration took place very slowly to give an equilibrium mixture of (II) and (III) (as shown by i.r. and u.v. spectroscopy); none of the conjugated acetylene (Ib) was formed.

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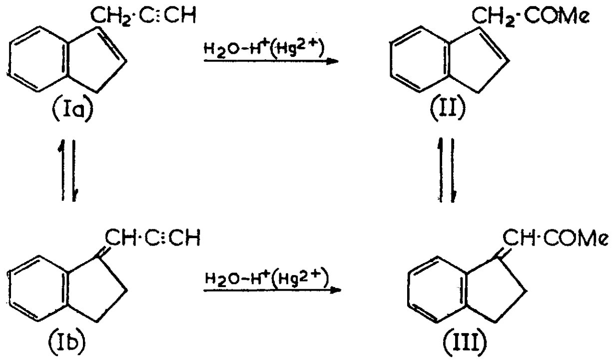
[1] R. A. Raphael, 'Acetylenic Compounds in Organic Chemistry,' Butterworths, London, 1955.

[2] R. N. Beale, *Nature*, 1956, **178**, 37.

Since the ketone (II) could not be isolated, we studied the isomerization of a similar system. Nothing was known about the acid-catalyzed isomerization of 3-benzylindene (Va) although Bergson *et al.*[3] had found that in a base-catalyzed equilibrium between (Va) and 1-benzylindene the former is preferred; our experiments confirmed this result and no 1-benzylideneindane (VIa) was formed. Only relatively weak bases were required to establish the equilibrium *via* the resonance-stabilized cyclopentadienyl anion,[3] although only with strong bases (*e.g.* potassium amide on alumina [4]) was a slow isomerization of (Va) to (VIa) observed.



Rapid isomerization took place when (Va) was boiled in ethanol–water (3 : 1) with 1% of sulphuric acid; (Va) was distilled off and isomeric 1-benzylideneindane (VIa) was crystallized from the residue. The conditions for this isomerization were identical with those used for the hydration of (Ia) although without the addition of mercuric sulphate which had no effect on the isomerization of the hydrocarbons. No side products were detected and the equilibrium was reached within 8 hr. (the data summarized in Table 2 were obtained after 16 hr.). The quantitative determination of the composition of the equilibrium mixture by gas chromatography showed the presence of 66·6% of (Va) and 33·4% of (VIa).

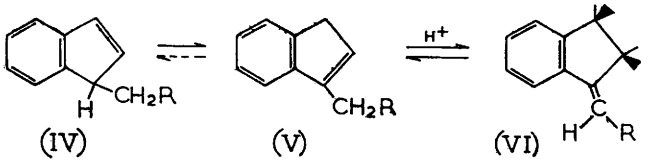
TABLE 2

Physical properties of C_9H_7–CH_2R (V) and C_9H_8=CHR (VI) and equilibrium composition at 90° [catalyst, 1% H_2SO_4; for 24 hr. in alcohol–water (8 : 2)]

	M.p.		B.p./mm.		U.v. spectrum				
					$\lambda_{max.}$ (mμ)		$\varepsilon_{max.}$		(VI) (%) *
R	(I)	(II)	(I)	(II)	(I)	(II †)	(I)	(II †)	At equil.
Ph	Liq.	75°	116°/5		250	316	10,500	30,000	33(33)
o-MeC_6H_4	Liq.		168/4		252	[310]	9000	[12,000]	18·5
p-MeC_6H_4	Liq.	83	178/1		252	319	9700	27,000	39(43)
2,4,6-$Me_3C_6H_3$	82°		142/1		252		10,200		6
Me	Liq.	Liq.	104/15		251	252	10,000	9000	3(3)

* The values in parentheses ( ) are those obtained from the reverse isomerization of (VI) into (V). † The values in brackets [ ] refer to the bands which were detected in the u.v. spectra of the equilibrium mixtures of (V) and (VI): pure (VI) was not isolated. In this case, the value of ε was estimated by measuring the relative concentration of (V) and (VI) by g.l.c. The ε was therefore not very precise.

Although, at first, it seems surprising that (Va) is the preferred isomer in the equilibrium, since the the double bond in (Va) is conjugated with only one phenyl ring and that in (VIa) with two phenyl rings (see u.v. spectra in Table 1), a model of (Va) reveals the strained conformation of the eclipsed methylene groups.



R
a; Ph
b; o-MeC_6H_4
c; p-MeC_6H_4
d; 2,4,6-$Me_3C_6H_2$
e; Me

Table 2 shows the influence of steric and electronic effects of substituents on the phenyl ring on the equilibrium composition. An *ortho*-substituent lowers the concentration of (VI) an effect which is pronounced with the mesityl derivative (VId) where both *ortho*-positions are substituted. The model shows that interaction of the methyl group with the methylene group of the indane ring does not permit a planar system. In addition, it shows that the *cis*-isomer exhibits more severe steric hindrance than the *trans*-isomer: one methyl group strongly interacts with one of the aromatic hydrogens of the indane group. This conformation does not permit, therefore, the coplanarity of the phenyl group and the indane group. With the *o*-tolyl derivative only one configuration is possible without steric hindrance of coplanarity. Its formation demands a higher activation entropy than with benzene derivatives which have unsubstitued *ortho*-positions.

The electron-donating effect of the *para*-methyl group in the *p*-tolyl derivative increases only slightly the amount of (VI) in the equilibrium mixture. Since no essential stabilization of the intermediate carbonium ion, or of the product, can be expected from a methyl substituent and only traces of ethylideneindane (VIe) were detected in the equilibrium mixture.

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[3] G. Bergson, *Acta Chem. Scand.*, 1963, **17**, 2691; A. M. Weidler, *ibid.*, p. 2724; G. Bergson and A. M. Weidler, *ibid.*, 1964, **18**, 1487.

[4] A. J. Hubert and H. G. Viehe, *J. Chem. Soc.* (*C*), 1968, 228.

The spectra of 1-benzylideneindanes are similar to those of stilbenes. The comparison of the i.r. spectrum of (VI) with that of (V) revealed the same kind of modification as was observed between the i.r. spectrum of (III) and the spectra of indene derivatives. The transition of the indene ring into a substituted indane was thus easily recognized by i.r. spectroscopy.

The u.v. spectra shows a bathochromic shift when compared with that of stilbene (see Tables 1 and 2). The presence of some absorption at a shorter wavelength [*ca.* 296 and 284 mμ (see also the band at 294 mμ in the u.v. spectrum of the ketone (III)] is perhaps an indication of the presence of *cis*- and *trans*-isomers (*cis*-stilbene absorbed at a shorter wavelength than *trans*-stilbene), but no resolution could be achieved by g.l.c. or t.l.c. The compound must therefore be considered as homogeneous.

The following τ values were observed in the n.m.r. spectrum of (Va): 6·8 (2H, benzylic) and 6·2 (CH$_2$ of the indene ring). The n.m.r. spectrum of (VIa) showed only one complex signal of 4 CH$_2$-protons at τ 7·25.

Since the ketone (III) is much more rapidly isomerized than the hydrocarbons (V) or (VI) the formation of the intermediate cation must be more favoured by the ketone group than by the phenyl group.

EXPERIMENTAL (In collaboration with M. Hubert and L. Kumps.

Prop-2-ynylindene.—Prop-2-ynyl bromide (1 mole in ether (100 ml.) was added to a solution of indenylsodium (1 mole) in liquid ammonia (1 l.) and the mixture was stirred overnight. After evaporation of the ammonia water and ether were added and the organic layer was separated, dried (Na$_2$SO$_4$): and the solvent was then distilled off. Fractionation gave 3-prop-2-ynylindene (50%), b.p. 74°/0·5 mm. Some diprop-2-ynylindene was present in the residue of distillation. The i.r. spectrum showed bands typical of acetylenic group at 3·5 and 4·7 μ; other characteristic bands were observed at 6·17, 6·84, 10·28, 10·9, 12·9, and 13·95 μ.

The n.m.r. spectrum showed that the 3-isomer was obtained [by prototropic rearrangement of the 1-isomer (Ia) which was the probable intermediate of the reaction but which was quickly isomerized in the basic medium]: the aromatic protons absorbed at 2·84, the methylenic protons of the prop-2-ynyl group at 6·85, the methylenic proton of the indene portion at 7·00, and the acetylenic proton at 8·05 p.p.m.

Isomerization of 3-Prop-2-ynylindene.—A mixture of prop-2-ynylindene (3 g.), alcohol (75 ml.), water (25 ml.), and sulphuric acid (1 ml.) was heated under reflux. The reaction was followed by u.v. spectroscopy; a band at 3·17 mμ slowly appeared. The i.r. spectrum showed the presence of the ketones (II) (C=O stretching at 5·83 μ) and (III) (C=O stretching at 5·95 μ) in the mixture. These first changes (both in i.r. and u.v. spectra) were observed after 7 hr. The reaction proceeded very slowly and after 24 hr. 20% of ketones were present. No bands in the i.r. or u.v. spectra were detected that could be attributed to the 1-phenylbut-1-en-3-yne system of (Ib).

1-Acetonylideneindane (III).—Prop-2-ynylindene (20 g.) was heated under reflux with a mixture of alcohol (300 ml.), water (100 ml.), sulphuric acid (10 ml.), and mercuric sulphate (2 g.) for 0·5—1 hr.

The mixture was cooled and extracted with ether; the extract was dried (Na$_2$SO$_4$) and the ether was distilled off. Fractionation of the residue gave a viscous liquid, b.p. 112—140/2·10^{-1} mm., from which crystals separated when it was set aside overnight at 0°; further crystals were obtained when pentane was added to the solution which was then cooled in solid carbon dioxide. The product was recrystallized from pentane, hexane, or light petroleum (b.p. 40—60), m.p. 54—56 (Found: C, 83·05; H, 7·15. Calc. for C$_{12}$H$_{12}$O: C, 83·7; H, 7·0%) (yield 25%).

The i.r. spectrum showed bands at 3·27w, 3·43w, 5·95, 6·25 6·78w, 6·94w, 7·0w, 7·35, 7·82w, 8·0, 8·42, 8·57, 10·4, 11·77, and 13·31 μ.

The oily residue obtained by evaporation of the mother liquors contained further quantities of (III) as shown by its i.r. spectrum. It also contained other ketonic material as shown by a strong band at 5·83 μ. The bands at 12·9 and 13·95 μ were also observed. It was not possible to purify this fraction but it probably contained some of the ketone (II) (together with other compounds).

Isomerization of 1-Acetonylideneindane (III).—1-Acetonylideneindane (III) (2 g.) was boiled in a mixture of alcohol (75 ml.), water (25 ml.), and sulphuric acid (1 ml.). Aliquots of this were poured into water and the mixture was extracted with hexane. I.r. spectroscopy showed absorption due to a carbonyl group (5·83 μ); the ratio of the intensity of this absorption to the intensity of the absorption due to 1-acetonylideneindane (III) (5·95 μ) remained, after the first 15 min., for 4 hr. With longer periods of heating (10 hr.) some decomposition occurred.

Benzylindene (V; R = Ph).—The isomer (V; R = Ph) was obtained by the addition of benzyl bromide (1 mole) to a solution of indenylsodium (1 mole) in liquid ammonia (1 l.); the mixture was stirred overnight. The ammonia was evaporated off and the residue was taken up in water and extracted with ether. The solvent was evaporated off and the residue was distilled under reduced pressure to give the product, b.p. 116°/5 mm. (yield 40%). The compound was mainly the 3-isomer (V; R = Ph) because of the presence of base which isomerized the 1-isomer (IV; R = Ph) during the work-up procedure. Some dibenzylindenes remained as a residue in the distilling flask. The properties and the n.m.r. spectrum of this compound have been previously discussed.[3]

Isomerization of 3-Benzylindene (V; R = Ph).—Benzylindene (34 g.) was heated under reflux in a mixture (670 ml.) of ethanol–water (75—90% ethanol to ensure a homogeneous reaction mixture) and sulphuric acid (6·7 ml.). Samples of the mixture were poured into water and the aqueous phase was extracted with hexane. The solution was dried (Na$_2$SO$_4$) and the hexane was evaporated off. The residue was analyzed by g.l.c. and u.v. spectroscopy. No further changes were observed after 8 hr. (The results summarized in Table 2 were obtained after a reaction period of 16 hr.) The bulk of the solution was poured into water and extracted with hexane; the solvent was evaporated off and the residue was fractionated with a spinning band column. 3-Benzylindene (20 g.) distilled at 116°/1 mm. The residue (10 g.) consisted of benzylideneindane which was crystallized from ethanol; yield 7·5 g. (24%), m.p. 73·5—75° (lit.,[5] 73·4—74·4°).

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[5] S. S. Hirsch, D. H. Lorenz, and E. I. Becker, *J. Org. Chem.*, 1958, **23**, 1829.

The i.r. spectrum showed bands at 6·14, 6·28, and 13·24 μ; bands which were observed at 6·24, 6·66, 13·0, 13·36, 13·55, 13·96, and 14·34 μ in the spectrum of 3-benzylindene had disappeared.

The n.m.r. spectrum showed the ten aromatic and olefinic protons at τ 2·8 and the four aliphatic protons at 7·25.

Isomerization of 1-*Benzylideneindane* (VI; R = Ph).—Pure 1-benzylideneindane was heated under reflux in a mixture of aqueous ethanol and sulphuric acid with the same conditions as described above. The isomerization was followed by g.l.c. The formation of benzylindene (V; R = Ph) was detected and the equilibrium was reached during 15 hr. (see Table 2).

Preparation of Substituted Benzylindenes (V; R = substituted Ph).—These compounds were prepared in a similar way to benzylindene by using substituted benzyl bromides instead of benzyl bromide. The yields and properties of these compounds are given in Tables 2 and 3.

TABLE 3

Yields * and analysis of $C_9H_7CH_2R$ (V) and $C_9H_8{=}CHR$ (VI)

R		Yield (%)	Found (%) C	Found (%) H	Calc. (%) C	Calc. (%) H
Ph	(V)	40	92·8	6·9	93·2	6·8
	(VI)	24 *	93·5	6·8		
o-MeC_6H_4	(V)	36	92·8	7·4	92·7	7·3
p-MeC_6H_4	(V)	68	92·3	7·3	92·7	7·3
	(VI)	30 *	92·3	7·3		
2,4,6-$Me_3C_6H_3$	(V)	55	91·5	8·3	91·9	8·1
Me	(V)	40	92·0	8·1	91·6	8·4
	(VI)	40 †	91·3	8·7		

* The yields of (VI) reported in this Table are those of pure isolated compounds while those reported in Table 2 are obtained from g.l.c. † Prepared by a Wittig reaction (see below).

Preparation of Substituted Benzylideneindane (VI; R = substituted Ph).—They were prepared in a similar way to benzylideneindane but in some cases they could not be purified (X = o-Me, and 2,4,6-Me_3). The yields and properties of these compounds are given in Tables 2 and 3.

Preparation of Ethylindene (V; R = Me).—This was prepared in a similar way to 3-benzylindene except that ethyl bromide was used instead of benzyl bromide. The n.m.r. spectrum shows signals at τ 2·7 (ArH), 3·8 (olefinic H), 6·7 (CH_2 of the indene group), 7·5 (CH_2 of the Et group), and 8·7 (Me).

Preparation of Ethylideneindane (VI; R = Me).—A solution of butyl-lithium (0·19 mole) in ether was added to a suspension of ethyltriphenylphosphonium bromide in ether. The mixture was stirred for 2 hr. and indanone (0·075 mole) was added. The mixture was stirred overnight and poured into ice–water. The organic layer was separated, the solvent was evaporated off, and the residue was distilled. The material contained 60% of ketone and 40% of (VI; R = Me). Pure (VI; R = Me) was obtained by chromatography of the mixture on silica gel and elution with hexene [alumina isomerized (VI) into (V) very rapidly] (Found: C, 91·3; H, 8·7%. Calc. for $C_{11}H_{12}$: C, 91·6; H, 8·4%). The purity of (VI; R = Me) was checked by g.l.c.; no (V; R = Me) was detected.

The n.m.r. spectrum shows signals at τ 2·95 (ArH), 4·1 [olefinic proton: this signal is more complex than the one corresponding to the olefinic proton of ethylindene (see above) because it is coupled with the methyl group (*J* 6·7 c./sec.) and with one of the CH_2 of the indane group (*J* 2·3 c./sec.)], 7·2 (the two CH_2 of the indane group) and 8·2 (Me).

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