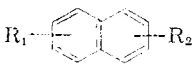
TABLE II



R_1	R_2	Reactants: Naphthol	Reactants: Mercaptan	Reactants: Catalyst	Isolation	Yield, %	M.p., °C.	Analyses, % Calcd./Found: C	H	S	Br
6-Br[11]	2-SCH_2COOH	6-Br, 2-OH (0.2 *m*)	$HSCH_2COOH$ (0.22 *m*)	TSA[h] (0.12 *m*)	[b]	91	163–165	48.5 48.6	3.0 3.1	10.8 10.9	26.9 26.6
H	1-SCH_2COOH	1-OH (0.2 *m*)	$HSCH_2COOH$ (0.22 *m*)	$NaHSO_4$ (0.15 *m*)	[b,d]	67	104–105 (111–112)[11]	66.1 65.8	4.6 4.7	14.7 14.7	
5-SCH_2COOH	1-SCH_2COOH	1,5-Diol (0.2 *m*)	$HSCH_2COOH$ (0.55 *m*)	TSA (0.12 *m*)	[b,e]	76	240–243 (250)[15]	54.5 54.6	3.9 4.0	20.8 20.9	
H[a]	2-SCH_3	2-OH (3.0 *m*)	CH_3SH (4.17 *m*)	TSA (0.87 *m*)	[c]	99	60–62 (63–64)[16]	Mixt. m.p. with known cmpd. not depressed[18]			
H[a]	2-SC_2H_5	2-OH (3.0 *m*)	C_2H_5SH (4.0 *m*)	TSA (0.87 *m*)	[c]	68	18–21 (16)[17]	. .		. .	
H[11]	2-$SC_5H_{11}(n)$	2-OH (0.2 *m*)	*n*-$C_5H_{11}SH$ (0.3 *m*)	TSA (0.06 *m*)	[c,f]	22[g]	16–17	78.4 78.2	7.8 7.5	13.9 14.2	
H	2-SC_6H_5	2-OH (0.2 *m*)	C_6H_5SH (0.25 *m*)	$NaHSO_4$ (0.17 *m*)	[c,d]	43[g]	50–51 (51.8)[19]	81.3 81.2	5.1 5.3	13.5 13.4	

[a] A 1.2-liter nickel autoclave was used. [b] The product was isolated in a manner similar to (2-naphthylthio)-acetic acid; hydrochloric acid was used instead of carbon dioxide to adjust the *p*H. [c] The product was isolated in a manner similar to 2-naphthyl *n*-dodecyl sulfide. [d] The product was recrystallized from alcohol. [e] The product was reprecipitated from alcohol with hydrochloric acid. [f] The product was recrystallized from hexane at −5–0° two times. [g] These are purified yields. [h] *p*-Toluenesulfonic acid.

The results of similar experiments with varying amounts of sodium hydroxide were: sodium hydroxide, 0.1 mole (18 hr.), 13% yield; 0.2 mole (23 hr.), 52% yield; 0.3 mole (23 hr.), 89% yield; 0.5 mole (24.5 hr.), 25% yield.

2-Hydroxy-1-naphthalenepropionic Acid.—2-Naphthol (28.8 g., 0.2 mole), ethylene glycol (25 ml.), sodium hydroxide pellets (12.0 g., 0.3 mole) and 3-mercaptopropionic acid (21.2 g., 0.2 mole) were stirred 17 hours at 150–170° under nitrogen. Hydrogen sulfide was evolved. The reaction mixture was diluted to one liter with water and clarified. The *p*H of the solution was made alkaline to Brilliant Yellow paper with hydrochloric acid. The precipitated 2-naphthol (10 g., 35%), was recovered by filtration. The filtrate was acidified and 15 g. of a tacky solid was removed by filtration (29% crude yield). Recrystallization from 1-butanol gave a white solid, m.p. 116–117° (lit.[20] m.p. 121°). The mixture m.p. with the known compound[20] was not depressed.

Acknowledgment.—The authors wish to thank Mr. O. E. Sundberg and his associates for the elemental analyses.

Bound Brook, N. J.

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(14) M. Schmidt to Kalle and Co., German Patent 414,853; *Frdl.*, **15**, 326 (1925).

(15) M. Schmidt and H. Rose to Kalle and Co., German Patent 380,712; *ibid.*, **14**, 927 (1923).

(16) F. Kehrmann and G. A. Sava, *Ber.*, **45**, 2898 (1912).

(17) F. Kroft and R. Schönherr, *ibid.*, **22**, 824 (1889).

(18) These compounds were prepared by the alkylation of 2-naphthalenethiol with dimethyl sulfate and diethyl sulfate. The 2-methylthionaphthalene melted at 60–61°. The 2-ethylthionaphthalene melted at 22–23°.

(19) E. Bourgeois, *Ber.*, **28**, 2327 (1895).

(20) A. F. Hardman, This Journal, **70**, 2119 (1948).

[Contribution from the Department of Chemistry, Massachusetts Institute of Technology]

The Synthesis of Derivatives of 1-Indanone and Indenone

By Herbert O. House, Vasken Paragamian, Rolland S. Ro[1] and David J. Wluka[1]

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Synthetic routes to indenone ethylene ketal, 2-ethylideneindanone and 2-(2-carboxyethyl)-indenone have been developed. The dehydrobromination of 2-bromo-2-ethylindanone has been found to yield predominantly the exocyclic unsaturated ketone.

We have been led to study preparative routes to 2-substituted indenones since certain members of this series can serve as starting materials for the synthesis of degradation products of the plant-growth stimulant, gibberellic acid.[2] This paper reports the results of our preliminary studies in this area.

Several methods for the conversion of 1-indanone (I) to indenone have been studied,[3] the most successful method being the conversion of the indanone to 2-acetoxy-1-indanone and then pyrolysis. Since 1-indanone (I) could be converted in high yield either to 2-bromo-1-indanone (II) or 2,2-dibromo-1-indanone by direct bromination,[4] we were led to explore methods for the dehydrobromination of the monobromo compound II. Although no isolable product was obtained by direct reaction of the bromo ketone II with a variety of bases, conversion of the bromo ketone II to the ketal III followed by reaction with potassium *t*-butoxide afforded the unsaturated ketal IV in an over-all yield of 46%. The ketal IV, unlike its parent ketone,[3b] was stable on storage and could be used directly as a dienophile in Diels–Alder reactions.[5]

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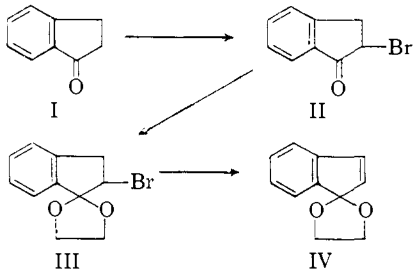
(1) Alfred P. Sloan Postdoctoral Fellow.

(2) For leading references, see B. E. Cross, J. F. Grove, J. MacMillan and T. P. C. Mulholland, *Proc. Chem. Soc.*, 221 (1958).

(3) (a) R. Stoermer and E. Asbrand, *Ber.*, **64**, 2796 (1931); (b) C. S. Marvel and C. W. Hinman, This Journal, **76**, 5435 (1954).

(4) (a) F. S. Kipping, *J. Chem. Soc.*, **65**, 501 (1894); (b) W. S. Johnson and W. E. Shelberg, This Journal, **67**, 1745 (1945); (c) C. L. Arcus and G. C. Barrett, *J. Chem. Soc.*, 2740 (1958).

(5) H. O. House, V. Paragamian, R. S. Ro and D. J. Wluka, This Journal, **82**, 1457 (1960).

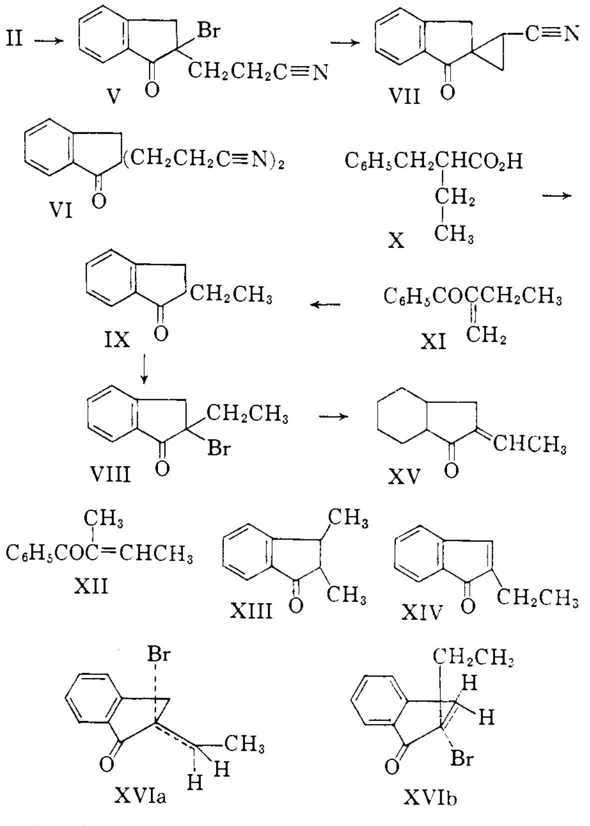


Since the direct dehydrohalogenation of α-halo ketones is usually more successful when the halogen atom is bonded to a tertiary carbon atom,[6] we investigated the behavior of two compounds of this type in the indanone series. The first, the nitrile V, was prepared by the cyanoethylation of the bromo ketone II. Attempts to prepare this bromo nitrile V by the initial monocyanoethylation of 1-indanone (I) were unsuccessful since the only product isolated from the Michael reaction was the dinitrile VI. The bromo nitrile V readily lost the elements of hydrogen bromide when treated with base to form a compound having the spectral properties of a 1-indanone derivative and a saturated nitrile. Thus, the product must be one of the diastereoisomeric forms of the keto nitrile VII. This structural assignment was in agreement with the nuclear magnetic resonance spectrum of the substance and with the fact that the product did not react with either dilute, aqueous potassium permanganate or bromine in carbon tetrachloride.

In order to avoid this competing ring-closure reaction, the dehydrobromination of 2-bromo-2-ethyl-1-indanone (VIII) was investigated. 2-Ethyl-1-indanone (IX) was prepared both by the cyclization of 2-benzylbutyric acid (X)[7] and by the cyclization of 2-ethylacrylophenone (XI) in the presence of either concentrated sulfuric acid[8] or polyphosphoric acid. We investigated the latter cyclization with particular care since the possibility existed that the original olefin XI[9] may have isomerized completely or in part to 2-methylcrotonophenone (XII) prior to cyclization.[8] Such isomerization would result in the formation of 2,3-dimethylindanone (XIII) rather than 2-ethylindanone (IX). The indanone samples obtained by both routes had identical infrared spectra. Both fractional distillation and gas chromatography of the product obtained by cyclization of 2-ethylacrylophenone (XI) suggested that the product was homogeneous. Both indanone samples formed the same crystalline monobromo derivative VIII and the same 2,4-dinitrophenylhydrazone in high yield. We conclude, therefore, that acid-catalyzed cyclization of the olefin XI is accompanied by little, if any, isomerization to the unsaturated ketone XII.

As a possible route to 2-(2-carboxymethyl)-indanone, ethyl 3-benzoyl-3-butenoate was prepared by the formation and decomposition of the Mannich base of ethyl β-benzoylpropionate. However, because of the poor yield (9%) of the unsaturated ester obtained, this reaction sequence was not explored further.

The bromo ketone VIII was readily dehydrobrominated by boiling γ-collidine to form a mixture consisting of 24% 2-ethylindenone (XIV)[10] and 76% of an isomeric crystalline solid. The infrared, ultraviolet and nuclear magnetic resonance spectra of the crystalline product were all consistent with its formulation as 2-ethylideneindanone (XV). The unsaturated ketones XIV and XV were not readily interconverted by acid since the two ketones formed different 2,4-dinitrophenylhydrazones. Furthermore, a sample of 2-ethylindenone (XIV) was not isomerized to the ethylidene compound XV under the conditions of the dehydrobromination indicating that the ratio of products obtained is the result of a rate-controlled process. The predominant direction of dehydrohalogenation of the bromo ketone VIII is explicable in terms of the transition states XVI for bimolecular elimination. Only in the transition state XVIa leading to the exocyclic olefin XV can a relatively strain-free *trans* coplanar arrangement of the atoms involved be attained.



Consideration of the ready cyclization of α-substituted cinnamic acids to indenones, especially if a

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[6] For example, see E. W. Warnhoff and W. S. Johnson, THIS JOURNAL, 494 (1953).

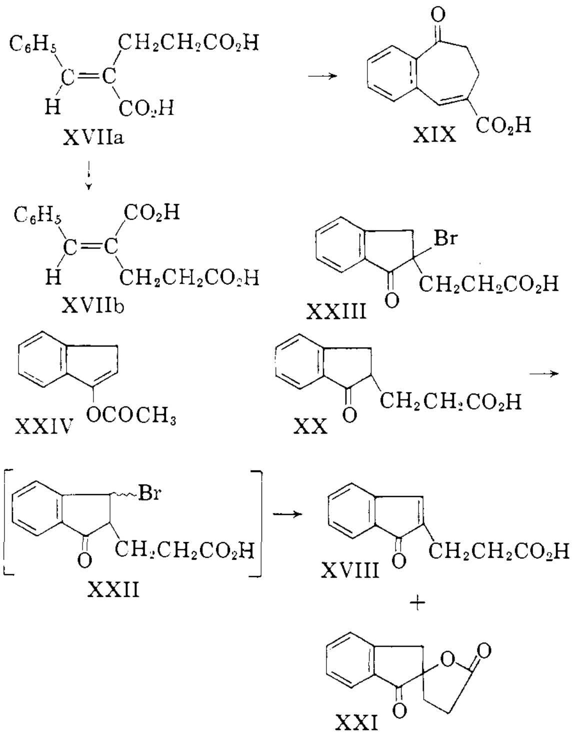
[7] J. Leuchs and G. Kowalski, *Ber.*, **58**, 2822 (1925).

[8] (a) J. H. Burckhalter and R. C. Fuson, THIS JOURNAL, **70**, 4184 (1948); (b) J. Colonge and G. Weinstein, *Bull. soc. chim. France*, 462 (1952). In both studies the 2-ethylindanone obtained was characterized as its semicarbazone. The additional characterization of this product described in this paper was undertaken because the alternative cyclization product, 2,3-dimethylindanone, and its semicarbazone are not described in the literature.

[9] We have presented evidence for the structure of this olefin previously; see H. O. House, D. J. Reif and R. L. Wasson, THIS JOURNAL, **79**, 2490 (1957).

[10] For the preparation and characterization of the ketone see (a) R. Stoermer and G. Voht, *Ann.*, **409**, 47 (1915); (b) H. O. House and D. J. Reif, THIS JOURNAL, **79**, 6491 (1957).

derivative of *cis*-cinnamic acid is employed,[10-12] prompted us to study the cyclization of the α-benzylideneglutaric acids (XVII). The condensation of benzaldehyde with diethyl glutarate as previously described[13] afforded a poor yield (15%) of a crystalline acid, m.p. 175–177°, with an ultraviolet spectrum comparable to *trans*-α-ethylcinnamic acid,[10] permitting the assignment of the *trans* structure XVIIa. Since we had observed earlier[10] the ready isomerization of substituted cinnamic acids in the presence of mineral acid, the *trans*-acid XVIIa was treated with polyphosphoric acid in the hope that isomerization and subsequent closure of a five-member ring to form the indenone XVIII would be more rapid than closure of a seven-membered ring to form the ketone XIX. However, the hope was not realized, the only product isolated being an acid having properties compatible with structure XIX. Irradiation of the *trans*-acid XVIIa with ultraviolet light produced a mixture from which both the starting *trans*-acid XVIIa and a new, isomeric acid, m.p. 135–137°, were isolated. The new acid, which has ultraviolet absorption comparable to *cis*-α-ethylcinnamic acid,[10] has been assigned the *cis* structure XVIIb. An attempt to prepare the desired indenone XVIII by reaction of the *cis*-acid XVIIb with polyphosphoric acid was not successful.



The desired 2-(2-indenonyl)-propionic acid (XVIII) was obtained from the saturated acid XX. The propionic acid derivative XX was obtained by the cyclization of α-benzylglutaric acid in the presence of anhydrous hydrogen fluoride as previously described.[14] Attempts to achieve this cyclization in the presence of polyphosphoric acid or aluminum chloride were not successful, an insoluble, high melting material being obtained instead of the desired indanone XX.[15] The reaction of the indanone XX with N-bromosuccinimide afforded a mixture of bromo acids. Both theoretical arguments[16] and previous experimental work[17] lead to the prediction that the major products of this radical bromination should be the diastereoisomers of structure XXII. The crude mixture of bromo acids from the bromination reacted readily with γ-collidine in ether solution to form the desired indenone XVIII accompanied by an isomeric neutral product which may be assigned the γ-lactone structure XXI from its spectral properties. Both the ease and the direction of this dehydrobromination as compared with the dehydrobromination of 2-bromo-2-ethylindanone (VII) indicated that the mixture of bromo acids was at least partially composed of the β-bromo ketones XXII. Our experiments do not permit a decision as to whether the lactone XXI was derived from the unsaturated acid XVIII or from the α-bromo ketone XXIII present in the bromo acid mixture.

In order to explore an alternative route to β-bromoindanone derivatives, indanone (I) was converted to its enol acetate XXIV by reaction with isopropenyl acetate. However, our attempts to isolate a pure substance from the reaction of the enol acetate with N-bromosuccinimide were unsuccessful.

Experimental[18]

1-Indanone (I).—The reaction of 110 g. (0.73 mole) of hydrocinnamic acid with 1 kg. of polyphosphoric acid at 70–85° for 1.5 hr. afforded, after distillation of the organic product, 84 g. (87%) of 1-indanone, m.p. 40–41° (lit.[19] m.p. 39.5–41°), with infrared absorption[20] at 1710 cm.$^{-1}$ (conj. C=O in a five-membered ring) and ultraviolet maxima[20] at 244 mμ (ε 11,200), 287 (ε 2,800) and 294 (ε 2,700). The residue from the distillation crystallized from ethanol as yellow needles of 2-(1-indanylidene)-1-indanone, m.p. 144.5–145° (lit. m.p. 142–143°,[21] 148°[22]), yield 7.5 g. (8.3%). The product exhibits infrared absorption[23] at 1685 (conj. C=O) and 1620 cm.$^{-1}$ (conj. C=C) with ultraviolet maxima[24] at 239 mμ (ε 8,300), 247 (8,600) and 344 (30,900).

Bromination of 1-Indanone.—The reaction of a solution of 40 g. (0.3 mole) of 1-indanone in 4 l. of ether, cooled to 0°, with 48 g. (0.3 mole) of bromine yielded 60.5 g. (96%) of crude, solid **2-bromoindanone (II)** of adequate purity for further transformation. Recrystallization of a portion of the material from petroleum ether afforded the pure bromo-

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[11] W. S. Johnson and G. H. Daub, *Org. Reactions*, **6**, 1 (1951).

[12] H. Stobbe and O. Horn, *Ber.*, **41**, 3983 (1908).

[13] R. Fittig and S. Roedel, *Ann.*, **282**, 338 (1894).

[14] M. F. Ansell and D. H. Hey, *J. Chem. Soc.*, 1683, 2874 (1950).

[15] The cyclization of α-benzylglutaric anhydride in the presence of aluminum chloride previously has been reported to form the indanone derivative XIX in poor yield accompanied by a polymer; see J. v. Braun and G. Manz, *Ann.*, **468**, 258 (1929).

[16] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 384.

[17] R. L. Huang and P. Williams, *J. Chem. Soc.*, 2637 (1958).

[18] All melting points are corrected and all boiling points are uncorrected. The infrared spectra were determined with either a Baird, model B, or a Perkin-Elmer, model 21, infrared recording spectrophotometer fitted with a sodium chloride prism. The ultraviolet spectra were determined with a Cary recording spectrophotometer, model 11 MS. The gas chromatograms were obtained with an 8 mm. × 215 cm. column packed with Dow Silicone Fluid No. 550 suspended on 50–80 mesh ground firebrick. The microanalyses were performed by Dr. S. M. Nagy and his associates and by the Scandinavian Microanalytical Laboratory.

[19] J. Koo, This Journal, **75**, 1891 (1953).

[20] Determined as a solution in chloroform.

[21] F. S. Kipping, *J. Chem. Soc.*, **65**, 496 (1894).

[22] E. D. Bergmann and R. Corett, *J. Org. Chem.*, **23**, 1507 (1958).

[23] Determined as a solution in carbon tetrachloride.

[24] Determined as a solution in 95% ethanol.

ketone, m.p. 37–38.5° (lit. m.p. 38–39°,[4a] 38.5–40°[4c]), which exhibited infrared absorption[20] at 1725 cm.$^{-1}$ (conj. C=O in a five-membered ring and adjacent to a halogen atom) and ultraviolet maxima[20] at 254 mμ (ϵ 12,300) and 293 (2,600).

The addition of 33 g. (0.21 mole) of bromine to a solution of 13 g. (0.1 mole) of 1-indanone in 100 ml. of chloroform afforded the crude dibromo ketone. Recrystallization from ethanol afforded the pure **2,2-dibromoindanone**, m.p. 133–134° (lit.[25] m.p. 132°).

Indenone Ethylene Ketal (IV).—A solution of 105 g. (0.5 mole) of 2-bromoindanone, 31 g. (0.5 mole) of ethylene glycol and 0.2 g. of *p*-toluenesulfonic acid in 800 ml. of benzene was refluxed for 4 days, the water being separated continuously as it was formed. Two additional 10-g. quantities of ethylene glycol were added during the reaction period. The resulting reaction mixture was concentrated, washed with two portions of aqueous sodium bicarbonate and then distilled under reduced pressure. The crude bromo ketal, collected at 95–105° (3.5 mm.), amounted to 89 g. (70%). The infrared spectrum[20] of the crude product exhibited almost no absorption at 1725 cm.$^{-1}$ indicating the absence of any appreciable amount of unchanged bromo ketone. A solution of the crude bromo ketal (89 g. or 0.35 mole) in 100 ml. of *t*-butyl alcohol was treated with a solution of 0.5 mole of potassium *t*-butoxide in *t*-butyl alcohol and the resulting mixture, which became deep-purple in color, was stirred for 3 hr. and then poured into ice-water. The organic product was extracted with ether, a small amount of dark insoluble material being removed by filtration. The ether extract was washed with water, dried over magnesium sulfate and distilled. The ketal, collected at 79–80° (0.15 mm.), amounted to 40 g. (46% based on the 2-bromoindanone) of colorless liquid, n^{28}D 1.5699, which solidified when cooled and melted at 21°. The product, which gave a negative Beilstein test for halogen, absorbs strongly in the infrared[23] at 1000 and 1050 cm.$^{-1}$ (C–O of a ketal)[26] and exhibits no band in the 6 μ region attributable to a carbonyl function; the ultraviolet spectrum[24] exhibits a maximum at 276 mμ (ϵ 2,800) with intense end absorption.

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.89; H, 5.76.

2,2-Bis-(2-cyanoethyl)-indanone (VI).—To a solution of 13.2 g. (0.1 mole) of 1-indanone and 3 drops of 40% aqueous benzyltrimethylammonium hydroxide in 100 ml. of *t*-butyl alcohol was added, dropwise and with stirring over a period of 90 min., a solution of 5.3 g. (0.1 mole) of acrylonitrile in 50 ml. of *t*-butyl alcohol. The temperature of the reaction mixture was kept below 30° throughout the addition. A portion of the crude dicyano ketone separated from the reaction mixture as a yellow oil. The residual solution was poured into water containing a few drops of hydrochloric acid and extracted with ether. The ether extract was washed with water, dried over magnesium sulfate and concentrated. Recrystallization of the crude organic products from ethanol afforded 9.2 g. (77% based on the acrylonitrile) of the pure dicyanoethylindanone, m.p. 87–89°. Concentration of the mother liquors afforded 6 g. (45% recovery) of crude 1-indanone, m.p. 32–33°. The dicyano ketone exhibits infrared absorption[20] at 2225 (C≡N) and 1700 cm.$^{-1}$ (conj. C=O in a five-membered ring) and has ultraviolet maxima[24] at 249 mμ (ϵ 15,300), 291 (2,780) and 297 (2,820).

Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92; N, 11.76. Found: C, 75.65; H, 5.90; N, 11.75.

The Cyanoethylation of 2-Bromoindanone (II).—To a solution of 21 g. (0.1 mole) of 2-bromoindanone and 8 g. (0.15 mole) of acrylonitrile in 50 ml. of *t*-butyl alcohol was added 10 g. of a 40% aqueous solution of benzyltrimethylammonium hydroxide. The resulting mixture was stirred at room temperature for 2 hr., diluted with water and extracted with ether. After the ether extract had been dried over magnesium sulfate and concentrated, the residue was taken up in ethyl acetate and decolorized with Norit. Fractional crystallization of the products from ethyl acetate–petroleum ether mixtures afforded **2-bromo-2-(2-cyanoethyl)-indanone (V)** as white needles, m.p. 93.5–94.5°, and the **keto nitrile VII** as white crystals, m.p. 153–154°. The reaction of a solution of 900 mg. (0.0034 mole) of 2-bromo-2-(2-cyanoethyl)-indanone in 40 ml. of *t*-butyl alcohol with one equivalent of potassium *t*-butoxide for 1 hr. at room temperature with subsequent appropriate manipulation afforded 300 mg. (48%) of the keto nitrile VII, m.p. 153–154°, which was shown to be identical with the product obtained from the cyanoethylation reaction by a mixed melting point determination.

The bromo keto nitrile V exhibits infrared absorption[20] at 2250 (C≡N) and 1715 cm.$^{-1}$ (conj. C=O in a five-membered ring and adjacent to a halogen atom) and has ultraviolet maxima[20] at 255 (12,800) and 297 mμ (ϵ 2,500).

Anal. Calcd. for $C_{12}H_{10}BrNO$: C, 54.57; H, 3.81; N, 5.30; Br, 30.26. Found: C, 54.87; H, 3.89; N, 5.44; Br, 30.23.

The keto nitrile VII has infrared absorption[27,28] at 2250 (C≡N) and 1705 cm.$^{-1}$ (conj. C=O in a five-membered ring) and ultraviolet maxima[20] at 247 mμ (ϵ 15,500), 288 (2,640) and 296 (2,600). The nuclear magnetic resonance spectrum[20,29] of the product has a peak at -111 sec.$^{-1}$ (aromatic C–H), a singlet at $+56$ sec.$^{-1}$ (CH_2 adjacent to a benzene ring and bonded to a carbon atom bearing no hydrogen atoms) and series of four or five partially resolved peaks in the region $+107$ to $+120$ sec.$^{-1}$ (adjacent CH and CH_2 groups) but no peak attributable to vinyl hydrogen atoms. The ratio of the area of the peak at $+56$ sec.$^{-1}$ to the area of the series of peaks in the region $+107$ to $+120$ sec.$^{-1}$ is 2 to 3.04. The product does not decolorize aqueous potassium permanganate or a solution of bromine in carbon tetrachloride.

Anal. Calcd. for $C_{12}H_9NO$: C, 78.67; H, 4.95; N, 7.65; mol. wt., 183. Found: C, 78.82; H, 5.12; N, 7.58; mol. wt., 213 (Rast).

Ethyl 3-Benzoyl-3-butenoate.—A solution of 41.2 g. (0.2 mole) of ethyl β-benzoylpropionate, 24.5 g. (0.3 mole) of dimethylamine hydrochloride, 13.5 g. (0.15 mole) of trioxane and 1 ml. of concentrated hydrochloric acid in 100 ml. of ethanol was refluxed for 23 hr. during which time an additional 13.5 g. (0.15 mole) of trioxane was added. The resulting mixture was concentrated and poured into dilute aqueous hydrochloric acid. The neutral and acidic components of the reaction mixture were removed by extraction with ether. From this extract appropriate manipulations afforded 23.5 g. (57% recovery) of unchanged ethyl β-benzoylpropionate, b.p. 156–162° (6 mm.), n^{26}D 1.5135, and 5.15 g. (14.5%) of β-benzoylpropionic acid, m.p. 114–116.5°. The acidic aqueous solution from the reaction mixture was saturated with potassium carbonate and extracted with ether. After the ethereal solution had been dried over magnesium sulfate and concentrated, distillation of the residual Mannich base afforded 4 g. (9.2%) of the crude unsaturated ester, b.p. 150–156° (8 mm.). Redistillation of this product yielded the pure unsaturated ester, b.p. 123.5–124.5° (0.3 mm.), n^{27}D 1.5252–1.5263, yield 3.99 g. (9.2%), which absorbs in the infrared[23] at 1737 (unconjugated ester C=O), 1662 (conjugated ketone C=O) and 988 cm.$^{-1}$ ($C{=}CH_2$ adjacent to a carbonyl group)[30] and has an ultraviolet maximum[24] at 247 mμ (ϵ 11,000).

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.74; H, 6.53.

2-Ethylindanone (IX). A. From 2-Ethylacrylophenone (XI).—2-Ethylacrylophenone[9,31] (33.93 g. or 0.21 mole) was added, dropwise and with stirring, to 80 ml. of concentrated sulfuric acid. By the time the addition was complete the temperature of the reaction mixture had risen to 80°. The mixture was allowed to cool with stirring for 90 min. and then poured into 850 ml. of water and extracted with ether. After the ethereal solution had been dried over magnesium sulfate and concentrated, distillation of the

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(25) F. S. Kipping, *J. Chem. Soc.*, **65**, 501 (1894).

(26) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1958, p. 116.

(27) Determined as a suspension in a potassium bromide pellet.

(28) Determined as a Nujol mull.

(29) Determined at a frequency of 40 mc. with a Varian Associates high-resolution nuclear magnetic resonance spectrometer, Model V 4300B. The position of the peaks are expressed as cycles per second relative to the proton resonance of water, a positive shift denoting a shift in the direction of decreasing resonance frequency at constant magnetic field strength.

(30) For examples and leading references see ref. 9.

(31) The gas chromatogram of the product, b.p. 122° (18 mm.), n^{24}D 1.5258, prepared as previously described (ref. 9), exhibited only one peak.

residue yielded 24.52 g. (72.1%) of liquid, b.p. 140–141° (18 mm.). Gas chromatographic analysis of the product indicated the presence of 98% 2-ethylindanone and 2% 2-ethylacrylophenone. The comparable reaction of 5.57 g. (0.034 mole) of 2-ethylacrylophenone with 25 ml. of polyphosphoric acid for 2 hr. with no external heating yielded 3.43 g. (61.8%) of liquid product, b.p. 136–144° (18 mm.), $n^{27}\text{D}$ 1.5350–1.5403, which was composed of 86% 2-ethylindanone and 14% 2-ethylacrylophenone. Distillation of the combined products through an 18-in. spinning-band column separated the 2-ethylacrylophenone, b.p. 120–122° (18 mm.), $n^{31}\text{D}$ 1.5209, and the pure 2-ethylindanone, b.p. 143° (18 mm.), $n^{31}\text{D}$ 1.5420 (lit. b.p. 144° (18 mm.),[7] 127° (12 mm.),[8b] $n^{20}\text{D}$ 1.5455,[8a] $n^{22}\text{D}$ 1.5457[8b]). The 2-ethylindanone exhibits infrared absorption[23] at 1715 cm.$^{-1}$ (conj. C=O in a five-membered ring) and has ultraviolet absorption[24] maxima at 245 (12,500) and 291 mμ (broad) (ε 2,500). Reaction of 0.3 g. (0.019 mole) of the ketone with a slight excess of 2,4-dinitrophenylhydrazine in 25 ml. of ethanol containing 2 ml. of concentrated sulfuric acid formed **2-ethylindanone 2,4-dinitrophenylhydrazone**, m.p. 172–175°, yield 0.54 g. (82%), which crystallized from an ethanol–ethyl acetate mixture as red crystals, m.p. 176–177°, yield 0.48 g. (72%).

Anal. Calcd. for $C_{17}H_{16}N_4O_4$: C, 59.99; H, 4.74; N, 16.46. Found: C, 59.93; H, 4.82; N, 16.70.

B. **From α-Ethyl-*trans*-cinnamic Acid.**—A solution of 2 g. (0.011 mole) of α-ethyl-*trans*-cinnamic acid in 15 ml. of ethanol was hydrogenated at room temperature and atmospheric pressure in the presence of 220 mg. of platinum oxide catalyst. The hydrogen uptake ceased after the absorption of 99.2% of the theoretical amount of hydrogen. The reaction mixture was filtered, concentrated and distilled through a short-path still at 8 mm. with a pot temperature of 180° (lit.[32] b.p. 168° (14 mm.)). The crude **2-benzylbutyric acid (V)**, amounting to 1.45 g. (72%), exhibits infrared absorption[23] at 1700 cm.$^{-1}$ (carboxyl C=O) with no absorption in the region 1610–1630 cm.$^{-1}$ (conj. C=C). A mixture of 1.35 g. (0.0076 mole) of the α-benzylbutyric acid and 20 ml. of polyphosphoric acid was heated to 90° with stirring for 1.5 hr. and then cooled and poured into water. The ether extract of the organic product was washed successively with water, aqueous sodium bicarbonate and water and then dried over magnesium sulfate. After concentration of the extract, distillation of the residue through a short-path still afforded 0.75 g. (63%) of 2-ethylindanone, $n^{28}\text{D}$ 1.5441. The infrared spectrum and the gas chromatogram of this product are identical with those obtained from the 2-ethylindanone sample prepared from 2-ethylacrylophenone. The product formed a 2,4-dinitrophenylhydrazone, m.p. 176–177°, in 84% yield which was identical with the 2-ethylindanone 2,4-dinitrophenylhydrazone derivative, previously described, as shown by a mixed melting point determination and the identity of the infrared spectra of the two samples. In addition this 2-ethylindanone sample formed a 2-bromo-2-ethylindanone sample, m.p. 60–61°, which did not depress the melting point of a sample of this bromo ketone prepared as subsequently described.

2-Bromo-2-ethylindanone (VIII).—To a solution of 12.13 g. (0.076 mole) of 2-ethylindanone (prepared from α-ethylacrylophenone) in 80 ml. of carbon tetrachloride was added, dropwise and with stirring, a solution of 12.2 g. (0.077 mole) of bromine in 75 ml. of carbon tetrachloride. The bromine reacted as it was added with the evolution of hydrogen bromide. The resulting reaction mixture was washed with aqueous sodium bisulfite, also by aqueous sodium bicarbonate and then dried over calcium chloride and concentrated. The residual crude bromo ketone, which amounted to 15.64 g. (86.5%), crystallized in standing. Two recrystallizations from petroleum ether afforded the pure bromo ketone as white prisms, m.p. 60–61.5°, yield 9.46 g. (52.5%). The infrared spectrum[23] of the product exhibits absorption at 1725 cm.$^{-1}$ (conj. C=O in a five-membered ring and adjacent to a halogen atom) and the ultraviolet spectrum[24] has maxima at 255 (12,100) and 300 mμ (ε 2,300).[33]

Anal. Calcd. for $C_{11}H_{11}BrO$: C, 55.25; H, 4.64; Br, 33.42. Found: C, 55.20; H, 4.65; Br, 33.50.

2-Ethylideneindanone (XV).—A solution of 7 g. (0.029 mole) of 2-bromo-2-ethylindanone and 4 g. (0.033 mole) of γ-collidine was heated to 175°[34] for 30 min. and then cooled and diluted with benzene. Filtration separated 5.82 g. (98.5%) of γ-collidine hydrobromide. The filtrate was washed successively with dilute hydrochloric acid, aqueous sodium bicarbonate and water and then dried over magnesium sulfate and concentrated. The gas chromatogram of the crude, neutral product (4.2 g. or 89%) indicated the presence of 24% 2-ethylindenone (XIV) and 76% 2-ethylideneindanone (XV). Distillation of the crude product afforded fractions, yield 3.32 g. (72%), b.p. 135–148° (9 mm.), $n^{21}\text{D}$ 1.5795 to 1.5868, all of which crystallized on cooling. Recrystallization of the entire distillate from petroleum ether separated 2.13 g. (48%) of pure 2-ethylideneindanone as white needles, m.p. 49.5–50.5°. The infrared spectrum[23] of the product has bands at 1710 (conj. C=O in a five-membered ring) and 1660 cm.$^{-1}$ (conj. C=C exocyclic to a five-membered ring) and the product has an ultraviolet absorption[24] maximum at 265 mμ (ε 22,600). The nuclear magnetic resonance spectrum[23,29] has a singlet at −113 sec.$^{-1}$ (aromatic C–H), a series of three or four partially resolved peaks at −86 sec.$^{-1}$ (vinyl C–H adjacent to a methyl group), a singlet at +57 sec.$^{-1}$ (CH_2 adjacent to an aromatic ring and bonded to a carbon atom bearing no hydrogen atoms) and a doublet at +106 and +113 sec.$^{-1}$ (CH_3 adjacent to a vinyl C–H).

Anal. Calcd. for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.36; H, 6.16.

The reaction of 0.35 g. of 2-ethylideneindanone with a solution of a slight excess of 2,4-dinitrophenylhydrazine in 25 ml. of ethanol containing 2 ml. of concentrated sulfuric acid yielded 0.74 g. (98%) of **2-ethylideneindanone 2,4-dinitrophenylhydrazone**, m.p. 210–212°. After chromatography on alumina, the product crystallized from an ethanol–chloroform mixture as red crystals, m.p. 217–218°.

Anal. Calcd. for $C_{17}H_{14}N_4O_4$: C, 60.35; H, 4.17; N, 16.56. Found: C, 60.14; H, 4.33; N, 16.52.

A 0.21-g. (0.0013 mole) sample of 2-ethylindenone was mixed with 0.16 g. (0.0013 mole) of γ-collidine and 0.27 g. (0.0014 mole) of γ-collidine hydrobromide and heated to 175° for 30 min. The crude product, amounting to 0.20 g., was isolated by the procedure previously described in the dehydrohalogenation of 2-bromo-2-ethylindanone. The gas chromatogram indicated the presence of only 2-ethylindenone in the recovered sample.

α-(2-Carboxyethyl)-*trans*-cinnamic Acid (XVIIa).—A mixture of 30 g. (0.16 mole) of diethyl glutarate and 17 g. (0.165 mole) of benzaldehyde in ethanolic sodium ethoxide prepared from 3 g. (0.13 g.-atom) of sodium and 200 ml. of ethanol was boiled under reflux with stirring for 6 hr. and then allowed to stand overnight. After the ethanol and unchanged benzaldehyde had been removed from the mixture by steam distillation, 20 g. (0.5 mole) of sodium hydroxide was added to the aqueous residue and the resulting mixture was boiled for 2 hr. The resulting mixture was extracted with ether and then acidified with hydrochloric acid. The precipitated solids (15.5 g.) were crystallized from water and then from an ethyl acetate–hexane mixture to separate 5.2 g. (15%) of the pure *trans*-acid, m.p. 175–177° (lit.[13] 175°). The infrared spectrum[27] of the *trans*-acid exhibits absorption at 1700 (carboxyl C=O), 1673 (conj. carboxyl C=O) and 1630 cm.$^{-1}$ (conj. C=C); the ultraviolet spectrum[24] has a maximum at 267 mμ (ε 17,700).[35]

2,3-Benz-2,4-cycloheptadien-1-one-5-carboxylic Acid (XIX).—A mixture of 3 g. (0.014 mole) of α-(2-carboxyethyl)-*trans*-cinnamic acid and 60 g. of polyphosphoric acid was heated to 80–90° for 30 min. and then poured into water and extracted with ether. The ethereal solution was washed with water, dried over magnesium sulfate and concentrated. Recrystallization from ethyl acetate and subsequently from an ethyl acetate–hexane mixture afforded the keto acid as white needles, m.p. 169–170°. A mixture of

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(32) J. von Braun, *Ann.*, **451**, 50 (1926).

(33) We are forced to conclude that the value of 45–46° reported for the melting point of 2-bromo-2-ethylindanone by Leuchs and Kowalski (ref. 7) is incorrect. These authors prepared 2-ethylindanone from α-benzylbutyric acid by a procedure comparable to the one reported in this paper.

(34) When the reaction mixture was heated to only 130° for 2 hr., 88% of the bromo ketone was recovered. The reaction appeared to occur rapidly only when the solution was heated above 165°.

(35) The corresponding values for α-ethyl-*cis*-cinnamic acid and α-ethyl-*trans*-cinnamic acid are 253.5 (12,300) and 266 mμ (ε 17,400), respectively (ref. 10).

the product with the starting diacid melted below 155°. The infrared spectrum[27] of the product has a band at 1670 cm.$^{-1}$ (conj. C=O) with a shoulder at 1690 cm.$^{-1}$ (carboxyl C=O) and a band at 1620 cm.$^{-1}$ (conj. C=C); the ultraviolet spectrum[24] has maxima at 240 mμ (ε 28,400), 281 (9,300) and 320 (5,700).

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.99. Found: C, 71.13; H, 5.03.

α-(2-Carboxyethyl)-*cis*-cinnamic Acid (XVIIb).—A solution of 2.16 g. of the *trans*-diacid (m.p. 175–177°) in 150 ml. of a benzene-ethyl acetate mixture was irradiated with the light from a low-pressure mercury vapor arc for 21.5 hr. After the solvents had been removed from the mixture, fractional crystallization from ethyl acetate separated 0.252 g. (12%) of the starting *trans*-diacid, m.p. 176–178.5°. Recrystallization of the mother liquors from a benzene–hexane mixture afforded 0.49 g. (23%) of the *cis*-diacid, m.p. 137–139°. The infrared spectrum[27] of the *cis*-acid has bands at 1718 (carboxyl C=O), 1667 (conj. carboxyl C=O) and 1626 cm.$^{-1}$ (conj. C=C) with a shoulder at 1700 cm.$^{-1}$; the ultraviolet spectrum[24] has a maximum at 255 mμ (ε 12,500).[27]

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.22; H, 5.51.

2-(2-Carboxyethyl)-indanone (XX).—Cyclization of α-benzylglutaric acid by the procedure of Ansell and Hey[14] yielded the desired keto acid, m.p. 106.5–108° (lit.[14] 106–108°) which exhibits broad absorption in the infrared[20] at 1710 cm.$^{-1}$ (conj. C=O in a five-membered ring and carboxyl C=O) and has ultraviolet maxima at 245 (13,700) and 291 mμ (ε 3,500).

2-(2-Indenoyl)-propionic Acid (XVIII).—A mixture of 10 g. (0.049 mole) of 2-(2-carboxyethyl)-indanone and 8.72 g. (0.049 mole) of N-bromosuccinimide in 200 ml. of carbon tetrachloride was irradiated and heated under reflux with a photo-flood lamp for 30 min. Filtration of the cool reaction mixture separated 4.6 g. (95%) of succinimide, m.p. 122–124°. After the filtrate had been concentrated to dryness under reduced pressure, a solution of the residue in 100 ml. of ether was treated with 50 ml. of γ-collidine and stirred for 6.5 hr. at room temperature. At this time the precipitated γ-collidine hydrobromide (7.0 g. or 71%) was removed by filtration and the filtrate was allowed to stand overnight. An additional 0.2 g. (2%) of γ-collidine hydrobromide separated during this time. The ethereal solution was washed successively with cold, dilute hydrochloric acid, water and aqueous potassium bicarbonate. The crude acidic product (3.9 g.) obtained from the bicarbonate extract was crystallized from acetone to give the desired indenone as yellow needles, m.p. 171–173°, yield 1.49 g. (15%). Recrystallization from acetone increased the melting point of the acid to 177.5–178.5°. The infrared spectrum[27] of the keto acid has a broad band at 1705 cm.$^{-1}$ (conj. C=O in a five-membered ring and carboxyl C=O) and the ultraviolet spectrum[24] has maxima at 236 mμ (ε 39,000), 242 (44,200) and 319 (1,370).

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.99. Found: C, 71.00; H, 4.97.

Distillation of the crude, neutral product (4.32 g.) from the dehydrobromination reaction through a short-path still at 0.1 mm. (pot temperature 180–185°) afforded 3.55 g. (36%) of the γ-lactone XXI which solidified on cooling. The pure lactone crystallized from methanol as white platelets, m.p. 86–88°. The product exhibits infrared absorption[20] at 1725 (conj. C=O in a five-membered ring) and 1782 cm.$^{-1}$ (C=O of an unconjugated γ-lactone) and ultraviolet maxima[24]) at 251 (13,100) and 296 mμ (ε 2,350).

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.28; H, 4.99. Found: C, 71.20; H, 5.25.

3-Acetoxyindene (XXIV).—A solution of 8 g. (0.061 mole) of 1-indanone and 50 mg. of *p*-toluenesulfonic acid in 45 ml. of isopropenyl acetate was refluxed under a fractional distillation column for 3 hr. during which time 17 ml. of distillate containing acetone was removed. The resulting reaction was neutralized with sodium bicarbonate, diluted with ether, washed with water and dried over sodium sulfate. After the ether solution had been concentrated, distillation of the residue afforded 9.7 g. (92%) of the enol acetate as a colorless liquid, b.p. 77–85° (0.2 to 0.25 mm.), which crystallized when cooled. Two recrystallizations of the product from petroleum ether afforded the pure enol acetate as colorless needles, m.p. 48.5–49.5°, which exhibits infrared absorption[23] at 1770 cm.$^{-1}$ (C=O of an unconjugated enol ester) and has an ultraviolet maximum[36] at 252 mμ (ε 2,520).

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.62; H, 5.96.

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(36) Determined as a solution in isoöctane.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Synthesis of Hexahydrofluorenone Derivatives

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The *cis* and *trans* isomers of hexahydrofluorenone have been synthesized by several routes. Reaction of either isomeric ketone with acrylonitrile or methyl acrylate yielded derivatives of 1a-(2-carboxyethyl)-*cis*-hexahydrofluorenone (XVI). This acid also was prepared from 2-(2-indenoyl)-propionic acid (XVII).

1,1a,2,3,4,4a-Hexahydrofluoren-9-one (I) has been prepared by cyclization of the acid chloride III of *trans*-2-phenylcyclohexanecarboxylic acid (II) in the presence of aluminum chloride[2] and by the acid-catalyzed cyclization of 1-cyclohexenyl phenyl ketone (VIII) in the presence of either polyphosphoric acid[3] or a mixture of phosphoric and formic acids.[4] In two cases[2,3] the same product, a solid which melted at 42° and formed a 2,4-dinitrophenylhydrazone melting at 190°, was formed. The cyclization of 1-cyclohexenyl phenyl ketone in the presence of formic and phosphoric acids gave a liquid ketonic product which formed a 2,4-dinitrophenylhydrazone melting at 158°.[4] The suggestion was offered that the liquid ketone was the *cis* isomer Ia and the material melting at 42° was the *trans* isomer Ib.

We first prepared hexahydrofluorenone by the method of Cook and Hewett.[2] The required *trans*-2-phenylcyclohexanecarboxylic acid (II) was obtained by reaction of *trans*-cinnamic acid with butadiene and then catalytic hydrogenation of the intermediate cyclohexene derivative.[5] When aluminum chloride was added to a carbon disulfide solution of the acid chloride III derived from II, the product obtained was the ketone Ia, m.p. 40–41°,

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