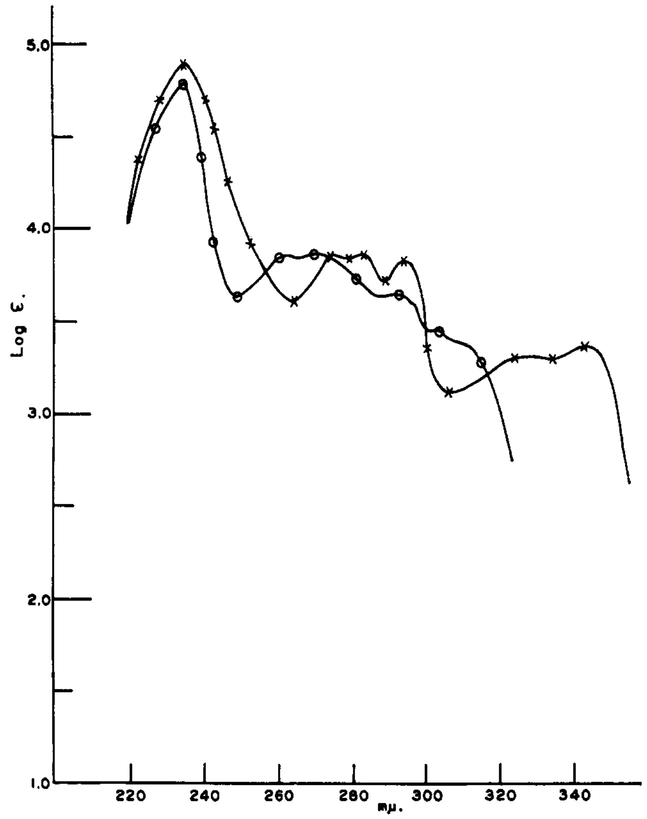

Fig. 1.—Ultraviolet absorption spectra: III ○—○—○; 1-methyl-17-dihydroequilenin, x—x—x.

was dried with anhydrous sodium sulfate and evaporated to dryness. The oily residue was dissolved in 200 ml. of methanol and a solution of 10 g. of sodium hydroxide in 20 ml. of water was added. The solution was refluxed for 1 hr., when 2 l. of water was added and the mixture was acidified with 2 *N* hydrochloric acid. After being collected, the resulting amorphous precipitate was dissolved in ether, dried, and treated with 1 g. of activated charcoal. The decolorized solution was concentrated to small volume and hexane was added when crystallization of fine needles started. Several recrystallizations from ether hexane yielded 2.1 g. (21%) of pure III, m.p. 163.5–164°, $[\alpha]_D$ +43.5°, $\lambda_{\max}^{\text{MeOH}}$ 235, 261, 270, 282, 293, and 314 mμ, log ε 4.78, 3.83, 3.84, 3.74, 3.63, and 3.28, respectively; $\lambda_{\max}^{\text{KBr}}$ 3.14, 6.19, 7.39, and 7.91 μ.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.71; H, 8.57. Found: C, 86.06; H, 8.44.

Acetate (IIIa).—The acetate of compound III was prepared with acetic anhydride and pyridine at room temperature.

It crystallized from methanol as plates, m.p. 82–83.5°, $[\alpha]_D$ + 45.9°, $\lambda_{\max}^{\text{MeOH}}$ 235, 263, 270, 284, 315 and 325 mμ, log ε 4.84, 3.83, 3.68, 3.76, 3.31, and 3.31, respectively; $\lambda_{\max}^{\text{KBr}}$ 2.94, 3.44, 5.69, 7.29, and 8.09μ.

Anal. Calcd. for $C_{22}H_{26}O_2$: C, 81.94; H, 8.13. Found: C, 82.05; H, 8.23.

3′,3′,5-Trimethyl-7-hydroxy-1,2-cyclopentenophenanthrene (IV).—A mixture of 2.5 g. of IIIa and 2 g. of 5% palladium-carbon was heated in an oil bath at 250–280° for 4 hr. The cooled reaction product was diluted with ether and the catalyst was removed by filtration. The filtrate was evaporated to dryness and the residual oil was saponified by being boiled for 1 hr. with a solution of 2 g. of sodium hydroxide in 5 ml. of water and 50 ml. of methanol. The reaction mixture was poured into 1 l. of water, acidified with 2 *N* hydrochloric acid, and extracted several times with ether. The combined extracts were washed with water and sodium bicarbonate solution, and then dried with anhydrous sodium sulfate. After concentration to a small volume, compound IV was precipitated with hexane. Two crystallizations from ether–hexane yielded 1 g. of pure product m.p. 144–145°, $[\alpha]_D$ 0, $\lambda_{\max}^{\text{MeOH}}$ 227, 262, 284, 296, and 307 mμ, log ε 4.23, 4.82, 4.13, 4.03, and 4.05, respectively.

Anal. Calcd. for $C_{20}H_{20}O$: C, 86.91; H, 7.29. Found: C, 86.57; H, 7.22.

Rearrangement of 2-Cyano-3-*t*-butyl-1-indenone

E. Campaigne and Donald R. Maulding[1]

Chemistry Laboratories, Indiana University
Bloomington, Indiana

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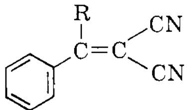
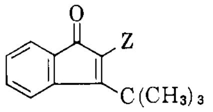
The formation of substituted indenones and indanones from the acid treatment of α-cyano-β-substituted cinnamonitriles I has been reported.[2] It was shown that, when the R groups in I were CH_3, C_2H_5, *i*-C_3H_7, or C_6H_5, cyclic ketoamides are produced, but that ring closure of I (R = *t*-C_4H_9) furnishes the cyano ketone IIa. Since the ketoamide IIb was desired, especially for ultraviolet study, several attempts to prepare it by hydration of IIa were made. Under several different acid conditions, the ketoamide was not formed; instead, a nitrile isomeric with IIa, as indicated by its elemental analysis and molecular weight determination, was isolated.



I

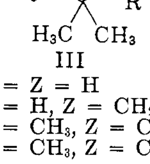


IIa. Z = CN
b. Z = CONH₂

Compound IIa is a yellow solid, m.p. 198°, while the isomer is white, and melted at 165°. In contrast to the infrared spectrum of IIa, which possessed peaks at 2252 cm.$^{-1}$ (CN) and 1720 cm.$^{-1}$ (CO), the spectrum of the white compound had a peak at 2250 cm.$^{-1}$ (CN), but the carbonyl vibrational frequency had been shifted to 1662 cm.$^{-1}$. A change in the ultraviolet spectrum was also observed. The spectrum of the white compound displayed a $\lambda_{\max}$ at 251 mμ (ε 19,300), as compared with $\lambda_{\max}$ 244 mμ (ε 35,000) for IIa.

Josier and Fuson[3] report that substituted 1-indenones show carbonyl absorption in the region of 1710–1740 cm.$^{-1}$ and α,β-unsaturated six-membered cyclic ketones near 1665 cm.$^{-1}$. Hassner and Cromwell[4] have found that 4,4-dimethyl-1-keto-1,4-dihydronaphthalene (IIIa) and 2-benzyl-4,4-dimethyl-1-keto-1,4-dihydronaphthalene (IIIb) have peaks in the infrared at 1665 cm.$^{-1}$ and 1662 cm.$^{-1}$, and $\lambda_{\max}$ values in the ultraviolet at 242 mμ (ε 10,600) and 252 mμ (ε 11,000), respectively.

The evidence presented thus far suggests a rearrangement of IIa involving ring expansion to 2-cyano-3,4,4-



III

a. R = Z = H
b. R = H, Z = $CH_2C_6H_5$
c. R = CH_3, Z = CN
d. R = CH_3, Z = $CONH_2$

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[1] Contribution no. 1105, taken in part from a thesis submitted to Indiana University in partial fulfillment of the requirements for the degree Doctor of Philosophy, June, 1962, by D. M., Bristol Predoctoral Fellow, 1960–1962.

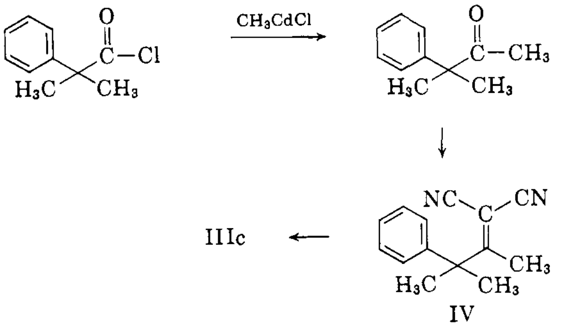
[2] E. Campaigne, G. F. Bulbenko, W. E. Kreighbaum, and Donald R. Maulding, *J. Org. Chem.*, **27**, 4428 (1962).

[3] M. L. Josier and N. Fuson, *Bull. soc. chim. France*, 389 (1952).

[4] A. Hassner and N. Cromwell, *J. Am. Chem. Soc.*, **80**, 893 (1958).

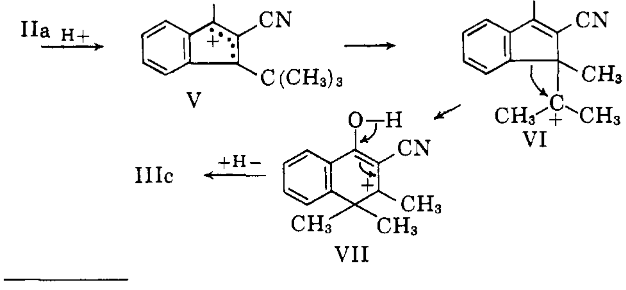
trimethyl-1-keto-1,4-dihydronaphthalene (IIIc), had occurred. Interpretation of the n.m.r. spectrum (60 Mc.) of the compound in question added convincing support favoring IIIc as the correct structure of the new product. It had an n.m.r. absorption peak centered at 8.39 τ, attributed to a *gem*-dimethyl group and a second peak (7.50 τ) of one-half intensity. The n.m.r. spectrum of IIa has a single resonance peak at 8.40 τ, representing the hydrogens on the tertiary butyl group.

An alternate synthesis of the cyano ketone IIIc was accomplished by the ring closure of the condensation product of malononitrile with 3-methyl-3-phenyl-2-butanone. Favorskiĭ,[5] *et al.*, prepared 3-methyl-3-phenyl-2-butanone by heating pivalophenone with zinc chloride at 320°, but a more direct approach, using the organocadmium synthesis,[6] gave a good yield of 3-methyl-3-phenyl-2-butanone. The condensation of the ketone with malononitrile was successful, but in low yield (26%) as expected from the considerable steric hindrance caused by the groups alpha to the carbonyl group. Ring closure of purified IV gave 2-cyano-3,4,4-trimethyl-1-keto-1,4-dihydronaphthalene (IIIC), which had an infrared spectrum and melting point identical with the rearranged product from IIa.



Conversion of IIa to IIIc was effected in concentrated sulfuric acid at room temperature and also by heating in polyphosphoric acid. The best yield of IIIc, however, was produced when IIa was heated in concentrated sulfuric acid on a steam bath for 10–15 minutes. When the reaction time was extended to two hours, rearrangement and hydration of the nitrile occurred, since 2-carbamoyl-3,4,4-trimethyl-1-keto-1,4-dihydronaphthalene (IIId) was isolated.

The formation of IIIc from IIa can be explained by the following reactions. Protonation of IIa leads to the formation of the resonance-stabilized carbonium ion V. This is the same type of intermediate as that proposed to explain the reaction sequence involved in the acid-catalyzed conversion of 2-carbamoyl-3-alkyl-1-indenones to 2-carbamoyl-3-alkylidene-1-indanones.[2] Since the tertiary butyl group prevents the formation of an indanone, IIIc is produced by an alternate path, namely methyl migration of the neopentyl carbonium ion V to yield the tertiary carbonium ion VI, ring expansion to give VII, followed by elimination of a proton.



Experimental

All melting points reported are corrected. The microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Indiana. Unless otherwise stated, all infrared spectra were recorded by a Perkin-Elmer Model 137 Infracord. The ultraviolet absorption spectra were determined in 95% ethanol with a Cary Model 14 recording spectrophotometer. The n.m.r. spectra were recorded in deuterated chloroform with a Varian Associates high-resolution n.m.r. spectrometer, Model V4300B.

Rearrangement of 2-Cyano-3-*t*-butyl-1-indenone (IIa).—One gram of IIa[2] was dissolved in 50 ml. of concentrated sulfuric acid and heated on a steam bath for 10–15 min. Upon pouring the deep red solution into 400 g. of ice, a yellow solid precipitated, which, when recrystallized from benzene–hexane, yielded 0.42 g. (42%) of white crystals, m.p. 164–165°. The infrared spectrum (Perkin-Elmer Model 137-G grating spectrophotometer) showed peaks at 3075 (aromatic CH), 3010 (aliphatic CH), 2250 (CN), and 1662 cm.$^{-1}$ (CO). The ultraviolet spectrum had a $\lambda_{\max}$ at 251 mμ (ϵ 19,200). The n.m.r. spectrum (60 Mc.) had a resonance peak at 8.39 τ and another at 7.50 τ, having one-half the intensity (tetramethylsilane as standard).

Anal. Calcd. for $C_{14}H_{13}NO$: C, 79.57; H, 6.20; N, 6.63; mol. wt., 211. Found: C, 79.35; H, 6.09; N, 6.63; mol. wt., 210–211 (Mechrolab vapor pressure osometer, Model 301A, determined in chloroform).

Dissolving 0.5 g. of IIa in 10 ml. of concentrated sulfuric acid and allowing to stand at room temperature for (a) 12 hr. and (b) 24 hr., then pouring over ice produced (a) 90 mg. (18%) and (b) 25 mg. (5%) of IIIc. Heating 0.5 g. of IIa dissolved in 20 ml. of polyphosphoric acid on a steam bath for 4 hr. yielded 100 mg. (20%) of IIIc after hyrolysis.

Rearrangement and Hydration of IIa.—One gram of the cyano ketone IIa was dissolved in 10 ml. of concentrated sulfuric acid and heated on a steam bath for 2 hr., then poured into 100 g. of ice. Extraction of the acidic solution with chloroform yielded an orange solid which, after washing with 5% sodium bicarbonate solution and recrystallization from aqueous ethanol, then benzene, gave 410 mg. (40%) of white crystals, m.p. 179–180°. $\nu_{\max}^{\mathrm{KBr}}$ 3520 (NH), 3205 (NH), 2985 (aliphatic CH), 1665 (CO), and 1640 cm.$^{-1}$ (amide CO).

Anal. Calcd. for $C_{14}H_{15}NO_2$: C, 73.36; H, 6.55; N, 6.15. Found: C, 73.14; H, 6.80; N, 6.22.

Preparation of α-Phenylisobutyric Acid.—While 75 g. (0.55 mole) of aluminum chloride and 200 ml. of dry benzene were being stirred in a 500-ml. three-necked round-bottomed flask, equipped with a condenser, calcium chloride drying tube, and stirrer, 42 g. (0.25 mole) of α-bromoisobutyric acid dissolved in 50 ml. of dry benzene was added by means of a dropping funnel. The mixture was stirred at room temperature for 1 hr., then refluxed for 6 hr. After standing overnight the dark solution was cautiously poured into one liter of 20% sulfuric acid and ice. The benzene layer was separated and washed with two portions of 10% sulfuric acid, one portion of water, and five 80-ml. portions of 5% sodium hydroxide. The dilute alkaline solution was treated with Norit and filtered into 400 ml. of 20% sulfuric acid. A white precipitate (33 g., 80%) which melted at 78–80° was collected. α-Phenylisobutyric acid has been reported to melt at 80–81°.[7]

Preparation of α-Phenylisobutyryl Chloride.—Freshly distilled thionyl chloride (15 g., 0.192 mole) was placed in a 500-ml. three-necked round-bottomed flask, equipped with a condenser, calcium chloride drying tube and exhaust tube. Fifteen grams (0.092 mole) of α-phenylisobutyric acid dissolved in 200 ml. of dry benzene was added by means of a dropping funnel. After the addition had been completed, the solution was refluxed for 30 min. Vacuum distillation of the crude acid chloride obtained after evaporating the excess thionyl chloride and benzene gave 15 g. of a clear liquid, b.p. 90° (2.0 mm.) [lit.,[8] 109° (13 mm.)].

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(5) A. Favorskiĭ, T. E. Zalesskaya, D. I. Rozanov, and G. U. Chelintzev, *Bull. soc. chim. France*, **3**, 239 (1936).

(6) D. A. Shirley, *Org. Reactions*, **VIII**, 28 (1954).

(7) A. Haller and E. Bauer, *Compt. rend.*, **155**, 1582 (1912).

(8) O. Wallach, *Chem. Zent.*, **II**, 1047 (1899).

Preparation of 3-Methyl-3-phenyl-2-butanone.—Six grams of magnesium metal turnings washed with a solution of iodine and ethyl ether was placed in a 500-ml. three-necked round-bottomed flask containing a Dry Ice condenser, stirrer, and gas inlet tube. One hundred milliliters of anhydrous ethyl ether was added and methyl bromide (b.p. 4.5°) was bubbled into the ether. The reaction started after adding a crystal of iodine and warming the ether. All the magnesium was dissolved after 2 hr. The Dry Ice condenser was replaced with a water-cooled condenser and 49 g. of cadmium chloride, previously dried to constant weight, was added. The slurry was refluxed for 50 min. until the solution gave a negative Gilman test. The ether was evaporated under nitrogen and 100 ml. of anhydrous benzene was added. With good stirring a solution of 25.7 g. (0.068 mole) of α-phenylisobutyryl chloride in 100 ml. of anhydrous benzene was added to the benzene solution of methylcadmium chloride. The solution was refluxed for 4 hr., cooled, and acidified with 20% sulfuric acid and ice. The benzene layer was separated and washed with 10% hydrochloric acid, 10% sodium hydroxide and water. After drying with sodium sulfate, the benzene solution was evaporated, and the resulting oil (19.1 g., 84%) distilled at 97° (0.5 mm.) [lit.,[5] 97–98° (11 mm.)]; $\nu_{\max}^{\text{KBr}}$ 2985 (with shoulders; aliphatic and aromatic CH) and 1701 cm.$^{-1}$ (CO). A vapor phase chromatogram (F and M 500 programmed temperature gas chromatograph with Carbowax 20 M column) showed the ketone was over 99% pure.

Anal. Calcd. for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.23; H, 8.55.

3-Methyl-3-phenyl-2-butylidenemalononitrile (IV).—Sixteen grams of 3-methyl-3-phenyl-2-butanone was dissolved in 150 ml. of anhydrous benzene and refluxed for 48 hr. with 8 g. of malononitrile, 3 g. of ammonium acetate, and 9 ml. of glacial acetic acid. Evaporation of the solvent gave an oil, which was distilled under reduced pressure. The first fraction collected (10.8 g.) was the starting ketone, b.p. 88–90° (0.2 mm.), and the second fraction, 5.2 g., b.p. 130–135° (0.25 mm.), had a peak in the infrared at 2220 cm.$^{-1}$. Redistillation gave an analytical sample collected at 133° (0.25 mm.).

Anal. Calcd. for $C_{14}H_{14}N_2$: C, 80.00; H, 6.67; N, 13.33. Found: C, 80.12; H, 7.03; N, 12.98.

Ring Closure of 1-Methyl-2-phenylisobutylidenemalononitrile (IV).—Two hundred milligrams of IV was allowed to react in 4 ml. of concentrated sulfuric acid at room temperature for 1 hr. A white solid precipitated after the dark green solution was poured into 40 g. of ice and allowed to stand overnight. Recrystallization from alcohol gave 152 mg. (78%) of white needles, m.p. 164–165°. The infrared spectrum was identical to IIIc and a mixture melting point showed no depression.

Acknowledgment.—We wish to acknowledge gratefully the support of this research by a grant from the Bristol Laboratories, Division of Bristol-Myers Company, Syracuse, New York. We wish also to acknowledge the support of the National Institutes of Health to Indiana University for the purchase of the high-resolution nuclear magnetic resonance spectrometer.

Reaction of *t*-Butoxy Radical with 4-Vinylcyclohexene

J. Reid Shelton and Antony Champ[1]

Department of Chemistry, Case Institute of Technology, Cleveland 6, Ohio

Received October 4, 1962

In continuation of a study of the reaction of free radicals with olefins, it became evident that further work was required to elucidate one phase of the work previously reported.[2]

The previous work had reported that the slow photolysis of di-*t*-butyl peroxide in 4-vinylcyclohexene yielded dehydrodimers and that the more rapid copper-induced decomposition resulted in both *t*-butyl vinylcyclohexenyl ethers and dehydrodimers. Reference was made to the work of Kharasch and Fono,[3] but it was also suggested that perhaps increased radical concentration resulting from more rapid peroxide decomposition might explain the production of the *t*-butyl vinylcyclohexenyl ether. Recent studies reported by Kochi[4] on the mechanism of the copper salt-catalyzed reactions of peroxides suggested the possibility of involvement of cupric *t*-butoxide in the reaction to form the ether provided the copper salt was sufficiently soluble in the reaction medium.

In order to test these two hypotheses, four reactions of di-*t*-butyl peroxide with 4-vinylcyclohexene were carried out at a temperature of 80°. These are written below in equation form with the major products indicated.

$$(t\text{-BuO})_2 + C_8H_{12} \xrightarrow[\text{heat}]{} t\text{-BuOH} + (C_8H_{11})_2 \quad (1)$$

$$(t\text{-BuO})_2 + C_8H_{12} \xrightarrow[\text{heat}]{\text{CuCl}_2} t\text{-BuOH} + t\text{-BuO-}C_8H_{11} + (C_8H_{11})_2 \quad (2)$$

$$(t\text{-BuO})_2 + C_8H_{12} \xrightarrow[\text{heat}]{h\nu} t\text{-BuOH} + (C_8H_{11})_2 \quad (3)$$

$$(t\text{-BuO})_2 + C_8H_{12} \xrightarrow[\text{heat}]{h\nu,\text{CuCl}_2} t\text{-BuOH} + (C_8H_{11})_2 \quad (4)$$

The rate of disappearance of di-*t*-butyl peroxide was observed to be the same in reactions 3 and 4 which was more rapid than 1 and 2. Comparison of 1 and 2 at 115° showed that reaction 2 is faster than 1. One also observes that reaction 2 in which the reactants are heated in the presence of copper salt is the only reaction to produce *t*-butyl vinylcyclohexenyl ether and that the photolysis reactions with or without cupric chloride produce no ether. In the case of reaction 2 the ether is formed in approximately the same amount as the dehydrodimer as determined by gas chromatography. One concludes from these data that the production of *t*-butyl vinylcyclohexenyl ether is definitely not a result of a radical concentration effect.

The formation of *t*-butyl vinylcyclohexenyl ether is visualized as occurring through a mechanism analogous to the one proposed by Kochi[4] in which a free radical R· is oxidized by a cupric salt, Cu(II)OX, to form ROX and Cu(I).

$$(t\text{-BuO})_2 + \text{Cu(I)} \longrightarrow t\text{-BuO}\cdot + t\text{-BuOCu(II)}$$
$$t\text{-BuO}\cdot + C_8H_{12} \longrightarrow t\text{-BuOH} + C_8H_{11}\cdot$$
$$t\text{-BuOCu(II)} + C_8H_{11}\cdot \longrightarrow t\text{-BuO-}C_8H_{11} + \text{Cu(I)}$$
$$2C_8H_{11}\cdot \longrightarrow (C_8H_{11})_2$$

Although cupric chloride was used in this study, some cuprous salt would soon be formed as a result of slow thermal decomposition of peroxide to produce free radicals which would initiate the above sequence. The production of dehydrodimer probably results from a coupling of vinylcyclohexenyl radicals.

Gas chromatography also indicated that a small amount of lower boiling materials was formed in the reactions. Infrared analysis was consistent with a product formed by attack of $CH_3\cdot$ radicals on 4-vinylcyclohexene. The spectra of two of the materials

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[1] Present address: Research Laboratories, Celanese Corp., Summit, N. J.

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[4] J. K. Kochi, *Tetrahedron*, **18**, 483 (1962).