

(0.058 mole) of benzaldehyde, 30 ml. of petroleum ether (b.p. 60–75°) and 12.4 g. of phosphorus pentoxide was allowed to stand protected by a drying tube for three days with occasional shaking. The yellow crystals, which had deposited, were then dissolved by boiling the mixture on a steam-bath. The resulting clear solution was then decanted from the brown gummy residue and the latter extracted by stirring with several portions of boiling petroleum ether. The combined solutions, which exhibited a strong green fluorescence, were then evaporated until crystallization began. Upon cooling, 11.1 g. (61%) of crude triaryl-methane deposited. These crystals, which melted at 90–97°, were recrystallized twice from petroleum ether and once from ethanol to furnish pure di-(2,5-dimethyl-3-thienyl)-phenylmethane melting at 96.5–97.5°.

Anal. Calcd. for $C_{19}H_{20}S_2$: C, 73.00; H, 6.46. Found: C, 72.98; H, 6.93.

1,2-Di-(2-furyl)-1,2-diphenylethane-1,2-diol.—Phenylmagnesium bromide was prepared from 5.4 g. (0.2 mole) of magnesium turnings and 31.4 g. (0.2 mole) of bromobenzene dissolved in 100 ml. of absolute ether and 100 ml. of dry benzene. This was quickly decanted from a trace of unused metal and cooled in another flask to 0° while protected by a drying tube. With mechanical stirring there was slowly added 9.5 g. (0.05 mole) of 2,2'-furyl. The dark

orange solution was stirred while being allowed to come to room temperature and was permitted to stand for two days protected by a drying tube. The mixture was then hydrolyzed by the addition of an iced, concentrated aqueous solution of 60 g. of ammonium chloride, the organic layer was washed twice with water and dried. The solvent was evaporated *in vacuo* at room temperature. The yellow residue was washed twice with petroleum ether (b.p. 30–60°) and dried. It weighed 16.3 g. and melted at 113–116°. After two recrystallizations from ethanol, the pure white crystals of pinacol melted at 130–131°. They assumed a yellow coloration upon prolonged standing.

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.27; H, 5.25. Found: C, 76.10; H, 5.11.

Rearrangement of 1,2-Di-(2-furyl)-1,2-diphenylethane-1,2-diol and Scission of the Pinacolone.—A 3.64-g. (0.01 mole) sample of the pinacol was treated as described above for the 2-thienyl analog. Sublimation of the acid fraction furnished 1.19 g. (98%) of white crystals melting at 118–120°. The melting point of a mixture of these with a sample of benzoic acid showed no depression.

Anal. Calcd. for $C_7H_6O_2$: C, 68.85; H, 4.96. Found: C, 69.13; H, 4.91.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

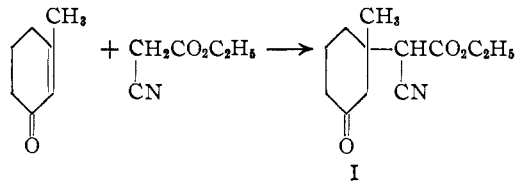
Structure of the Adduct of 3-Methyl-2-cyclohexenone and Ethyl Cyanoacetate. The Question of "Meta"- and "Para"- Bridged Rings

By P. R. SHAFER,¹ WILLIAM E. LOEB AND WILLIAM S. JOHNSON

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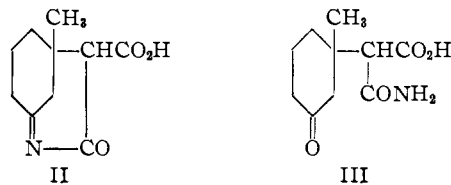
The structures assigned by Farmer and Ross to this adduct and to several products derived therefrom are challenged. A new structural interpretation, which does not necessitate the assumption of "meta"- and "para"- bridged ring intermediates, is given to these previously described transformations, and new supporting experimental evidence is provided.

Farmer and Ross² have described the reaction of ethyl cyanoacetate with 3-methyl-2-cyclohexenone in the presence of one equivalent of sodium ethoxide in excess ethanol. In addition to 3-methyl-2-cyclohexenylidencyanoacetic acid, they obtained a neutral oil b.p. 197° (2 mm.) in 21% yield. Since the latter was a ketonic adduct, $C_{12}H_{17}O_3N$, (semicarbazone, m.p. 166°) and failed to give a color with ferric chloride, they considered it to be the product I of a normal Michael reaction. Mild hydrolysis of the adduct with sodium carbonate



effected saponification to give the free cyano acid, $C_{10}H_{13}O_3N$, m.p. 106°, which on boiling for 15 minutes with 15% hydrochloric acid was practically quantitatively isomerized to a new acid, m.p. 181°. This same product was also produced in almost quantitative yield by somewhat longer treatment of I with aqueous alcoholic hydrochloric acid. On the basis of its mode of formation and further reactions (see below) Farmer and Ross assigned to the 181° acid the "meta"-bridged

structure II. In the present paper we challenge the structures I and II as well as those of several products derived therefrom, and present another interpretation of the transformations.

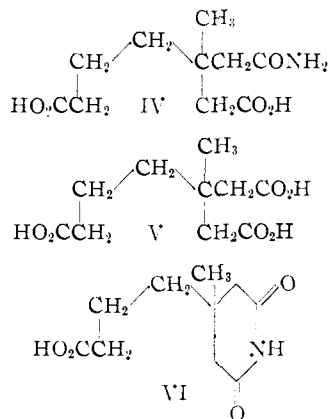


Farmer and Ross found their 181° acid II to be monobasic, to give an intense color with ferric chloride, and to react with bromine to give a dibromide, m.p. 186°, to which they assigned the molecular formula $C_{10}H_{13}O_3NBr_2$, but proposed no structure. On heating with 10% potassium hydroxide for 5 minutes, the 181° acid was hydrolyzed to a mixture of two nitrogen-containing acidic products formed in about equal amounts. One of these was a crystalline keto acid, $C_{10}H_{13}O_4N$, m.p. 151° (dec.), which was assigned the structure III. It gave no color with ferric chloride and reverted to the 181° acid II on heating with 15% hydrochloric acid. The other acidic product was a sirup, formulated as IV, since it was dibasic, and evolved ammonia upon prolonged heating with aqueous potassium hydroxide to give the known tribasic acid V, m.p. 125°, which was compared with authentic material prepared by independent synthesis. The oily dibasic acid IV, upon treatment

(1) Wisconsin Alumni Research Foundation Research Assistant, 1949–1950; U. S. Rubber Co., Fellow, 1950–1951.

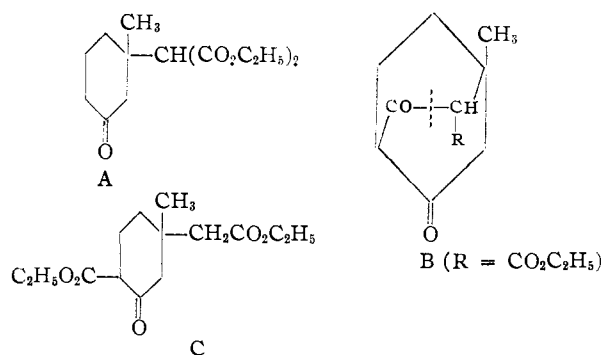
(2) E. H. Farmer and J. Ross, *J. Chem. Soc.*, 3233 (1926).

with hydrochloric acid, underwent cyclodehydration to the imide VI, m.p. 139°, which was compared with a specimen prepared from the authentic tribasic acid V. Both the 181° acid II and the 151° acid III gave the known tribasic acid V on prolonged alkaline hydrolysis.

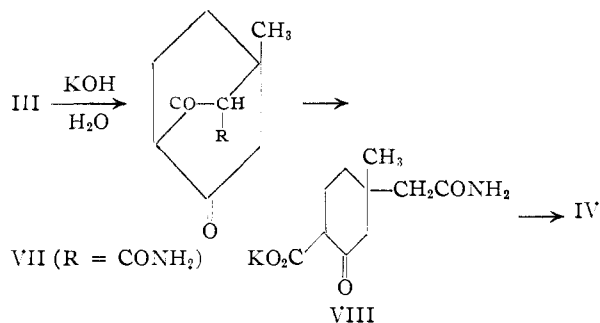
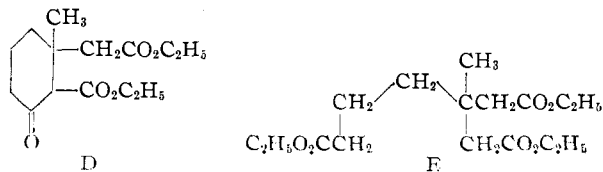


The reactions of the oily dibasic acid described above clearly establish its structure as IV. In order to rationalize the formation of IV from II, Farmer and Ross postulated that the first step was hydrolytic cleavage of the carbon-nitrogen double bond to give the keto acid III. By analogy to the "para"-bridging phenomenon which was proposed in the reaction of diethyl malonate with 3-methyl-2-cyclohexenone,³ the carboxylate group of III was presumed to condense with the reactive methylene group at C₆ to form the intermediary bicyclic compound VII, which undergoes hydrolytic cleavage to give VIII, this in turn hydrolyzing to give IV as follows

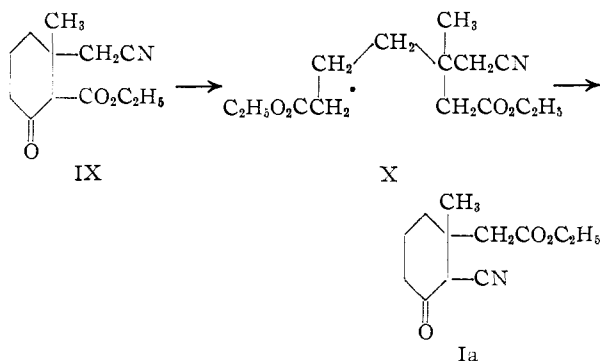
(3) E. H. Farmer and J. Ross, *J. Chem. Soc.*, 2358 (1923). The product C of this reaction was presumed to be formed from the normal Michael adduct A by an intramolecular ester condensation to produce the "para"-bridged intermediate B followed by alcoholysis at the point indicated (dotted line).



We submit the following alternate interpretation, which we prefer on the basis of the present study and on observations relating to the abnormal Michael reaction to be reported later. The expected product D of an abnormal Michael reaction is first produced. This compound then undergoes alcoholysis (reverse Dieckmann) to give the triester E which is known to cyclize to C (Farmer and Ross, as noted above.)



The interpretation of Farmer and Ross outlined above may be criticized *a priori* on a number of counts, some of which already have been noted by Bartrop,⁴ who has recognized certain weaknesses in the structure II. (1) The conditions employed for the initial condensation are those which favor abnormal rather than normal Michael addition.⁵ (2) Treatment of I, of the corresponding acid, of II,⁴ and of III with warm mineral acid would be expected to result in extensive decarboxylation. (3) The precedent cited⁶ for the formation of II is not valid. (4) The structure II violates Bredt's rule.⁴ (5) The structure II, being a derivative of a malonic semi-amide would not be expected to give a color with ferric chloride.⁴ (6) The condensation of a carboxylate anion with a reactive methylene group in aqueous alkali, III → VII, appears highly improbable.



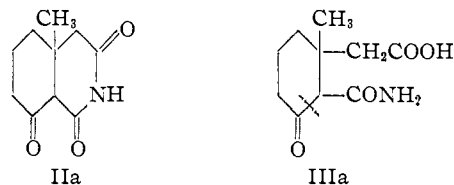
In the present work we have repeated a number of the experiments of Farmer and Ross, and have made additional studies, all of which have forced us to the conclusion that the Farmer and Ross adduct is not I but rather the α -cyano ketone Ia. The formation of Ia can be rationalized by the following sequence: (a) condensation of methylcyclohexenone and ethyl cyanoacetate in the

(4) Cf. J. A. Bartrop, *J. Chem. Soc.*, 399 (1947).

(5) J. A. Gardner and H. N. Rydon, *ibid.*, 48 (1938); R. Connor and D. B. Andrews, *THIS JOURNAL*, 66, 2713 (1934); R. Connor and W. R. McClellan, *J. Org. Chem.*, 3, 370 (1939).

(6) E. P. Kohler, A. Graustein and D. R. Merrill, *THIS JOURNAL*, 44, 2536 (1922); E. P. Kohler and B. L. Souther, *ibid.*, 44, 2903 (1922), showed that the normal Michael adduct of benzalacetophenone and methyl cyanoacetate cyclized rapidly and reversibly to the tetrahydropyridone under the influence of anhydrous halogen acids in non-solvent media. The behavior in aqueous medium was not mentioned, but in methanolic hydrogen chloride both the adduct and the cyclic product gave the same open chain dimethyl ester; and in glacial acetic acid containing sulfuric acid the adduct was converted to the corresponding dibasic acid. Unlike the 181° acid of Farmer and Ross, the tetrahydropyridone ring was not cleaved by dilute base; on the contrary, the ester group was saponified, and the resulting acid underwent decarboxylation on warming well below 130°.

manner of the abnormal Michael reaction⁵ to give IX; (b) alcoholysis (reverse Dieckmann) of IX to give X; (c) recyclization of X preferentially toward the methylene activated by the cyano group to give Ia. This structure is consistent with the solubility of the adduct in 10% potassium carbonate solution and regeneration on acidification, its formation of a semicarbazone, and its failure to give a color with ferric chloride under the usual conditions.⁷ These first and last properties are inconsistent with the structure IX which otherwise would be a suitable formulation of the adduct. The 106° acid produced on mild alkaline hydrolysis accordingly has the structure Ia (H in place of C₂H₅) which would not be expected to be particularly susceptible to decarboxylation. The acid treatment, on the other hand, could reasonably effect hydrolysis of the cyano to the carbamido group and the resulting amide acid would be expected to cyclize to the imide IIa which is hence considered to be the structure of the 181° "isomerized acid" (instead of II).



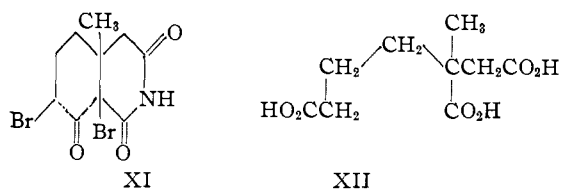
Consistent with the structure IIa are: (a) its formation from Ia or the corresponding acid on treatment with hydrochloric acid⁸; (b) its stability to mineral acid⁸; (c) its behavior toward titration as a monobasic acid, but failure (inconsistent with II) to dissolve in aqueous sodium bicarbonate; (d) its production of a strong coloration with ferric chloride (β -diketone-like structure); (e) its formation of a crystalline 2,4-dinitrophenylhydrazone of formula C₁₆H₁₇O₆N₅ (inconsistent with II); and (f) its behavior toward alkaline hydrolysis and toward bromination described below.

The alkaline hydrolysis of IIa evidently proceeds first to form IIIa, which therefore represents the structure of the 151° keto acid rather than III. IIIa would be expected to revert easily to IIa (see above), and the gas evolved on melting is undoubtedly water rather than carbon dioxide as thought by Farmer and Ross. The failure of IIIa to give a color with ferric chloride is similar to the case of the corresponding nitrile Ia. On more vigorous alkaline hydrolysis IIIa obviously cleaves at the point indicated (dotted line) to yield the dibasic acid IV of known structure.

Upon repeating the bromination of the 181° compound we observed that hydrogen bromide was evolved. The analysis is also in slightly better agreement with a product of substitution rather than addition. The dibromide thus is probably XI, which is favored over the alternate formula with a bromine attached to the nitrogen atom because the infrared spectrum still shows the N-H absorption.

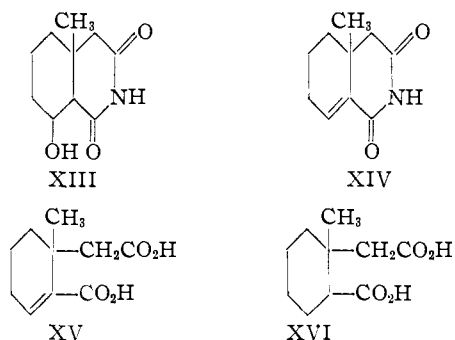
(7) Cf. the behavior of α -cyano ketones, v. Auwers, Th. Bahr and E. Frese, *Ann.*, **441**, 68 (1925).

(8) Cf. the conversion of glutaric half-acid nitriles into glutarimides, J. F. Thorpe and W. J. Young, *J. Chem. Soc.*, 936 (1900); P. H. Howles, J. F. Thorpe and W. Udall, *ibid.*, 942 (1900).



Evidence supporting the structure Ia was supplied by treatment of a solution of the adduct in potassium carbonate with potassium permanganate. Oxidation proceeded very rapidly at 0° to consume about five equivalents of oxidant, and β -carboxy- β -methylpimelic acid (XII), m.p. 147–148°, was produced in 80% yield. This acid was compared with an authentic specimen prepared by independent synthesis. The facile, highly selective oxidation is hard to reconcile with the structure I which at best would be expected to undergo oxidative fission between C₆ and C₁ as well as C₁ and C₂ to give a mixture of acids.

Conclusive evidence for the structures proposed in the present work was provided by reduction of the bicyclic imide IIa with sodium borohydride to give the crystalline hydroxy imide XIII, m.p. 184°, which gave no color with ferric chloride. Heating with dilute hydrochloric acid effected dehydration to the unsaturated imide XIV, m.p. 166°, λ_{\max} 226 m μ (log *E* 4.10). Prolonged alkaline hydrolysis of XIV afforded an unsaturated dibasic acid XV, m.p. 201°, λ_{\max} 214 m μ (log *E* 3.93),



which on catalytic hydrogenation yielded the known crystalline *cis*-1-methyl-2-carboxycyclohexane-1-acetic acid (XVI). This compound as well as its crystalline *trans* isomer, obtained by acid-catalyzed epimerization, was compared by mixed melting point and infrared determination with authentic material prepared by the method of Linstead and Millidge.⁹

Experimental¹⁰

Ethyl 1-Methyl-2-cyano-3-ketocyclohexaneacetate (Ia).—The condensation of 3-methyl-2-cyclohexenone¹¹ with ethyl cyanoacetate was carried out according to the method of Farmer and Ross.² Thus from 55 g. of ketone, 56.5 g. of ester and sodium ethoxide (from 11.5 g. of sodium) there was obtained 14.4 g. (13% yield) of the neutral adduct, b.p. 150–160° (0.3 mm.). Redistillation through a 30-cm. Vigreux column afforded 10.9 g. of pale yellow oil, b.p.

(9) R. P. Linstead and A. F. Millidge, *ibid.*, 478 (1936).

(10) Melting points are corrected for stem exposure. The ultraviolet spectra were determined on a Cary, Model 11MS, recording spectrophotometer. Infrared spectra were determined on a Baird recording spectrophotometer.

(11) Prepared by the method of L. I. Smith and G. F. Ronault, *This Journal*, **65**, 631 (1943).

123–124° (0.015 mm.). The product is reported to boil at 197° (2 mm.).²

The semicarbazone was formed rapidly in practically quantitative yield. The crude derivative was obtained as fine colorless needles, m.p. 166.8–167.1°. After two recrystallizations from ethanol the m.p. was 167.1–167.3° (reported² 166°). After the adduct had stood for two weeks, the crude semicarbazone, m.p. 163.5–163.7°, was obtained in only 85% yield.

Anal. Calcd. for C₁₃H₂₀O₃N₄: C, 55.70; H, 7.19. Found: C, 55.93; H, 6.89.

After it was discovered that the adduct was soluble in 10% potassium carbonate solution, a slightly modified procedure was developed, in which the desired product was separated from starting materials and tarry residues by use of this reagent, after the bicarbonate wash. The yield was not improved by this procedure, but the distillation was simplified. Variations in the reaction conditions from 60 hours at room temperature to 16 hours at steam-bath temperature did not affect the yield appreciably.

A solution of one drop of the freshly purified adduct in 1.5 ml. of ethanol gave no color upon addition of 10 drops of 1% ethanolic ferric chloride. On introduction of one-half a drop of pyridine, however, a red-purple color developed.

1,3,8-Triketo-10-methylperhydroisoquinoline (IIa).—This substance was prepared by the procedure of Farmer and Ross.² From 3.00 g. of Ia, heated first with 2.5 g. of potassium carbonate in 25 ml. of water, then further after adding 15 ml. of concentrated hydrochloric acid, there was obtained 2.43 g. of colorless crystalline imide, m.p. 176–177.5°. After recrystallization from ethyl acetate, the m.p. was 181.5–182° (reported² 181°). Repeated recrystallization of a sample from benzene gave colorless prisms, m.p. 183–183.6°, λ_{\max} 3.14 μ (Nujol mull).

Anal. Calcd. for C₁₀H₁₃O₃N: C, 61.52; H, 6.71. Found: C, 61.35; H, 6.46.

This product gave an intense purple color with 1% ethanolic ferric chloride. It failed to dissolve in aqueous or dilute methanolic 5% sodium bicarbonate solution, even upon warming. The imide dissolved in 10% potassium carbonate solution on warming to about 70°. Acidification of the solution with carbon dioxide reprecipitated the imide, m.p. 181–183°.

The 2,4-dinitrophenylhydrazone formed readily in practically quantitative yield, m.p. about 220–240° dec. Repeated recrystallization from a large volume of ethyl acetate, in which the derivative is only sparingly soluble, gave an orange microcrystalline powder, m.p. 246–248° dec. (introduced in bath at 230°).

Anal. Calcd. for C₁₈H₁₇O₆N₃: C, 51.20; H, 4.57. Found: C, 51.65; H, 4.46.

The dibromide was prepared according to the method of Farmer and Ross.² After two recrystallizations from chloroform it was obtained as colorless needles, m.p. 187.5–188° dec., vac. (introduced in bath at 180°) (reported² 186°), λ_{\max} 3.2; 3.24 μ (Nujol mull).

Anal. Calcd. for C₁₀H₁₁O₃NBr₂: C, 34.02; H, 3.14; Br, 45.28. Calcd. for C₁₀H₁₃O₃NBr₂: C, 33.83; H, 3.69; Br, 45.02. Found: C, 34.11; H, 3.19; Br, 45.4.¹²

Permanganate Oxidation of Ethyl 1-Methyl-2-cyano-3-ketocyclohexaneacetate (Ia).—A solution of 1.4 g. of potassium permanganate in 50 ml. of water was added dropwise with stirring to a mixture of 1.16 g. of the adduct Ia dissolved in 10 ml. of 10% potassium carbonate and 50 g. of ice. The permanganate color was discharged as rapidly as the solution was added, and manganese dioxide precipitated immediately. After 15 minutes the addition was complete, and the trace of permanganate remaining was reduced by adding a small amount of sodium bisulfite. The mixture was filtered and the manganese dioxide washed well with water. About 0.1 g. of potassium hydroxide was added to the combined filtrate and washings which were then concentrated on the steam-bath to a volume of about 10 ml. The cooled solution was acidified with 5% hydrochloric acid (to turn congo red blue), and repeatedly extracted with ether. The combined ether solutions were washed several times with saturated salt solution and then evaporated. The tan residue slowly solidified, and was rendered completely crystalline by trituration with a little ether. The

product amounted to 0.9 g., m.p. 147–148°, undepressed on admixture with an authentic sample of β -carboxy- β -methylpimelic acid, m.p. 147–148°. Recrystallization from benzene-ethyl acetate raised the m.p. to 148.7–149.3°, neut. equiv., 73.1 (calcd., 72.7).

β -Carboxy- β -methylpimelic Acid.—The trimethyl ester of this acid was prepared according to the method of Banerjee¹³ and purified by fractionation through a 30-cm. heated Vigreux column, b.p. 112–113° (0.2 mm.).

A mixture of 35.11 g. of the trimethyl ester and 200 ml. of concentrated hydrochloric acid was refluxed for 72 hours, cooled, made basic with sodium carbonate, filtered from traces of tar, and then acidified with concentrated hydrochloric acid to turn congo red blue. The triacid was recovered by extraction with ether and after removing this solvent the residue was dried by azeotropic distillation with benzene. The residual oil solidified after standing and an essentially quantitative yield (30 g.) of the crude tribasic acid was obtained, m.p. 140–144.5°. After two recrystallizations from benzene the m.p. was 147–148°.

Anal. Calcd. for C₉H₁₄O₆: C, 49.54; H, 6.47; neut. equiv., 72.7. Found: C, 49.83; H, 6.42; neut. equiv., 72.9.

1,3-Diketo-8-hydroxy-10-methylperhydroisoquinoline (XIII).—A solution of 1.35 g. of sodium borohydride in 45 ml. of methanol and 5 ml. of water was added to a suspension of 2.00 g. of the imide IIa in 50 ml. of methanol. The mixture bubbled vigorously, heat was evolved and the imide dissolved to produce a colorless solution. After standing for 30 minutes the solution was acidified with concentrated hydrochloric acid, and most of the alcohol removed by concentration in a current of nitrogen. When the total volume of the mixture was about 20 ml., water was added, and the cloudy suspension extracted with ethyl acetate. The solution was washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and concentrated. The residue amounted to 1.48 g. of a tan oil which crystallized on scratching, m.p. 180–183°. This material gave no color with alcoholic ferric chloride. Repeated recrystallization from benzene gave small colorless prisms, m.p. 183–184°.

Anal. Calcd. for C₁₀H₁₅O₃N: C, 60.89; H, 7.67. Found: C, 60.97; H, 7.50.

1,3-Diketo-10-methyl-1,2,3,4,5,6,7,10-octahydroisoquinoline (XIV).—A solution of 1.48 g. of the crude hydroxy imide XIII in 7.5 ml. of methanol, 7.5 ml. of water and 15 ml. of concentrated hydrochloric acid was boiled under reflux for 21 hours. During this treatment the solution turned quite dark in color, then light brown, and finally deposited a light tan crystalline product amounting to 0.45 g. The mother liquor was saturated with sodium chloride and extracted with chloroform. From the chloroform solution 0.9 g. of a tan oil was obtained which solidified on seeding with the crystalline material. Both fractions were combined and recrystallized from benzene to give 1.31 g. (97% yield) of colorless prisms, m.p. 165–165.5°, $\lambda_{\max}^{\text{EtOH}}$ 226 m μ (log *E* 4.10). Repeated recrystallization raised the m.p. to 165.5–166°. This material dissolved in dilute potassium hydroxide solution but was insoluble in 5% sodium bicarbonate solution. It decolorized potassium permanganate solution slowly. The once-recrystallized product was sublimed at 120–135° (0.01–0.05 mm.) for analysis, λ_{\max} 3.2, 3.24 μ (Nujol mull).

Anal. Calcd. for C₁₀H₁₃O₂N: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.85; H, 7.41; N, 7.85.

1-Methyl-2-carboxy- Δ^2 -cyclohexeneacetic Acid (XV).—A solution of 0.90 g. of the unsaturated imide XIV in 50 ml. of 20% potassium hydroxide solution was allowed to boil under reflux in a stainless steel flask for 52 hours when the evolution of ammonia had ceased. The solution was acidified with hydrochloric acid, and the cloudy mixture was extracted with ether continuously for 10 hours. Evaporation gave 0.51 g. of crude crystalline acid, m.p. 199–200°. Repeated recrystallization from water gave elongated prisms, m.p. 200.5–201°, $\lambda_{\max}^{\text{EtOH}}$ 214 m μ (log *E* 3.93). This compound decolorized a dilute solution of potassium permanganate.

Anal. Calcd. for C₁₀H₁₄O₄: C, 60.59; H, 7.12; neut. equiv., 99. Found: C, 60.21; H, 7.39; neut. equiv., 100.5.

(12) This analysis for Br was reported by Farmer and Ross, ref. 2.

(13) D. K. Banerjee, *J. Indian Chem. Soc.*, **17**, 453 (1940).

***cis*-1-Methyl-2-carboxycyclohexaneacetic Acid (XVI).**—A 0.056-g. sample of sublimed unsaturated acid XV, m.p. 197–198°, was dissolved in 18 ml. of purified (by refluxing over Raney nickel) 0.1% sodium hydroxide solution, and hydrogenated at room temperature and atmospheric pressure over 0.05 g. of 10% palladium-on-carbon (American Platinum Works) which had already been suspended in 10 ml. of water and equilibrated over hydrogen. After 20 hours of stirring the calculated amount of gas had been absorbed and no further reaction was occurring. The mixture was filtered and the filtrate and washings were concentrated to about 50 ml. Acidification with concentrated hydrochloric acid gave 0.0125 g. of colorless crystals, m.p. 160–167°. Concentration of the mother liquors gave a second crop of 0.0075 g., m.p. 160–167°, and further concentration gave two additional crops amounting to 0.027 g., m.p. 120–127°, possibly containing considerable of the *trans* isomer (see below). The first two crops were combined and recrystallized twice from water, m.p. 172–173.5°. Further recrystallization did not raise the m.p. There was

no depression of the m.p. on admixture with an authentic specimen of the *cis* acid XVI, m.p. 171.5–172.5° (reported⁹ 171.5–172°) prepared by the method of Linstead and Millidge.⁹ The infrared spectra of the two samples determined in Nujol mull were identical.

***trans*-1-Methyl-2-carboxycyclohexaneacetic Acid.**—A 0.02-g. sample of the *cis* isomer produced in the hydrogenation experiment described above was epimerized by heating with 10 ml. of concentrated hydrochloric acid for 16 hours at 200° according to the procedure of Linstead and Millidge.⁹

After two recrystallizations from water it melted at 133–134°. Further recrystallization did not change the m.p. There was no depression of the m.p. on admixture with authentic *trans* acid, m.p. 131.5–132.5° (reported⁹ 131–132°) obtained by isomerization of the authentic *cis* acid mentioned above. The infrared spectra of the two specimens of the *trans* acid determined in Nujol mull were identical except for slight irregularities which may be attributed to differences in impurities.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE PAINT DIVISION OF THE PITTSBURGH PLATE GLASS COMPANY]

Cyclopentenylphenols

BY ALFRED R. BADER

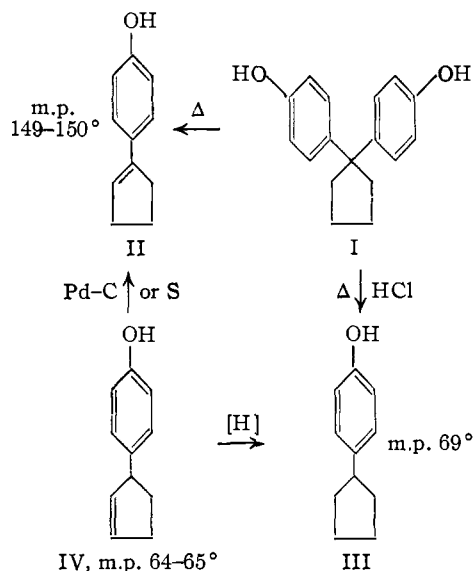
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The reaction of phenol with cyclopentadiene at 25° in the presence of phosphoric acid yields mainly *p*-2-cyclopentenylphenol IV, while *o*-2-cyclopentenylphenol VII is the major phenolic product at higher temperatures.

Cyclopentyl- and cyclopentenylphenols have hitherto been accessible only *via* cyclopentenyl chloride,¹ the Friedel-Crafts alkylation of phenol² and anisole³ with cyclopentanol and cyclopentanone, and the decomposition of *p*-cyclopentylidenediphenol (I).⁴

The only recorded attempt to alkylate phenol with cyclopentadiene appears to have been that of v. Braun and Kühn¹ who obtained viscous oils in the reaction catalyzed by hydrochloric acid.

The availability of cyclopentadiene and the hope of preparing unsaturated, non-conjugated phenols for isomerization studies prompted the reinvestigation of its reactions with phenol. At room temperature and with substantial quantities of phosphoric acid, *p*-2-cyclopentenylphenol IV is formed in ca. 70% yield. This is a crystalline solid, m.p. 64–65°, characterized by a *p*-nitrophenylurethan, m.p. 174°. The phenol IV can be isomerized by palladium-on-charcoal or by sulfur to the known⁴ *p*-1-



cyclopentenylphenol (II), melting at 149–150°, and hydrogenation of IV yields *p*-cyclopentadienylphenol (III), which had been reported to melt at 56°² and at 63–65°⁴ and which, when pure, melts at 69°.

When dicyclopentadiene and phenol are refluxed with a catalytic amount of phosphoric acid, the dimer reacts in part to yield the known⁵ solid phenoxydihydro-exo-dicyclopentadiene, V or VI, and a liquid isomer thereof, and in part decomposes to cyclopentadiene which then alkylates phenol in the ortho position. The identity of the crystalline ether with that prepared by Bruson and Riener by the sulfuric acid-catalyzed reaction of dicyclopentadiene with phenol at 30° was established by direct comparison, and by the preparation of identical di-

(5) H. A. Bruson and T. W. Riener, *THIS JOURNAL*, **68**, 8 (1946).

(1) J. v. Braun and M. Kühn, *Ber.*, **60**, 2551 (1927). Professor Martin G. Ettlinger has kindly pointed out that v. Braun and Kühn's *o*-2-cyclopentenylphenol probably was the product of C-alkylation rather than of Claisen rearrangement of phenyl cyclopentenyl ether as these authors believed. The ether, which these authors never had in hand, could not undergo normal rearrangement with inversion, for the transition state would be sterically improbable and would virtually violate Bredt's rule. The analogous 2-cyclohexenyl phenyl ether (J. W. Cornforth, G. K. Hughes and F. Lions, *J. Proc. Royal Soc. N. S. Wales*, **71**, 323 (1938); *C. A.*, **33**, 148 (1939), yields as the major products, phenol and cyclohexadiene. Furthermore, the cyclopentenyl ether of *o*-2-cyclopentenylphenol which v. Braun and Kühn apparently did have gave no 2,6-dicyclopentenylphenol on distillation, but cleaved to cyclopentadiene and *o*-2-cyclopentenylphenol. A direct C-alkenylation under conditions similar to those of v. Braun and Kühn is described by L. Claisen and E. Tietze, *Ber.*, **59**, 2344 (1926).

(2) German Patent 615,448.

(3) C. Mentzer, D. Molho and D. Xuong, *Bull. soc. chim.*, 263 (1948).

(4) J. v. Braun, E. Anton, W. Haensel and G. Werner, *Ann.*, **472**, 1 (1929).