hydroxide in 25 ml. of water and 0.3 g. (0.0012 mole) of $\Delta^{4a(10a)}$-dodecahydrophenanthrene-2,3-dicarboxylic anhydride (IX) was heated on a steam-bath for 10 minutes, the reaction mixture was neutralized carefully with 10% hydrochloric acid. The mixture was extracted with ether and the extracts were dried over magnesium sulfate. The dried ether solution was concentrated and cooled to yield 0.27 g. (85%) of slightly impure $\Delta^{4a(10a)}$-dodecahydrophenanthrene-2,3-dicarboxylic acid (X), m.p. 182–183°. Recrystallization from an ether–petroleum ether mixture gave an analytically pure sample, m.p. 184–185°.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.00; H, 7.99.

Dehydrogenation and Decarboxylation of $\Delta^{4a(10a)}$-Dodecahydrophenanthrene-2,3-dicarboxylic Anhydride (IX).—Simultaneous dehydrogenation and decarboxylation of 0.20 g. (0.0077 mole) of $\Delta^{4a(10a)}$-dodecahydrophenanthrene-2,3-dicarboxylic anhydride (IX) was carried out in the presence of 0.1 g. of a 10% palladium-on-carbon catalyst and 0.07 g. of a copper-chromite catalyst. When the mixture had been heated for 3.5 hours at 275°, 92 mg. (67%) of crude phenanthrene (XI), m.p. 80–89°, had sublimed to the cold finger of the dehydrogenation apparatus. Resublimation produced a fairly pure sample of phenanthrene (XI), m.p. 98–100°. A mixed melting point determination with an authentic sample of phenanthrene showed no depression.

$\Delta^{6a(12a),9}$-Tetradecahydrobenz[a]anthracene-8,11-dione (XII).—A solution of 1.08 g. (0.01 mole) of benzoquinone and 1.62 g. (0.01 mole) of 1,2-dimethylenedecalin (I) in 30 ml. of anhydrous ether was heated under reflux for 8 hours. When the reaction mixture was cooled, a white solid precipitated from the solution. The precipitate, which was removed by filtration, was recrystallized from absolute alcohol to yield 2.13 g. (79%) of white $\Delta^{6a(12a),9}$-tetradecahydrobenz[*a*]anthracene-8,11-dione (XII), m.p. 139.5–140.5°.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 80.00; H, 8.15. Found: C, 80.05; H, 8.09.

Ionic Polymerization of 1,2-Dimethylenedecalin (I).—In a test-tube, 2.1 g. of 1,2-dimethylenedecalin (I) was thoroughly mixed with approximately 5 g. of powdered Dry Ice and the mixture was cooled in additional Dry Ice. After a few drops of boron trifluoride etherate had been added, the mixture was stored for 3 days at −20° and then for 2 days at 5° before it was allowed to warm to room temperature. The viscous mixture was dissolved in benzene containing a trace of N-phenyl-β-naphthylamine and the resulting solution was poured into cold methanol. The light-tan precipitate was removed by filtration, washed thoroughly with methanol, and dried under partial vacuum to yield 1.21 g. (57%) of crude poly-1,2-dimethylenedecalin (XIII). Fractional precipitation of this crude polymer from a benzene solution into a large excess of methanol gave 0.22 g. of a white, powdery polymer, softening point 102–112°. A viscosity determination in a benzene solution with a modified Ubbelohde viscometer at 30° indicated an intrinsic viscosity of 0.03.

COLLEGE PARK, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

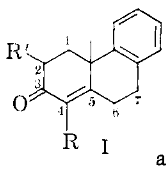
Hydrophenanthrenecarboxylic Esters[1]

BY ERNEST WENKERT AND BILL G. JACKSON

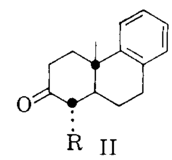
RECEIVED MAY 1, 1959

A synthetic route from hydrophenanthrones to the resin acids is developed. A rate-controlled formation of enolate ion of unsymmetrical ketones is described. The position of keto–enol equilibrium of cyclic β-ketoesters is discussed.

The ready availability of hydrophenanthrones Ia, IIa and III by standard synthesis or by any of three recently developed synthetic routes[2] and the easy access to hydrophenanthrenecarboxylic acids of various stereochemical configurations (IV)[3] made a conversion of any of the ketones into the acids most attractive. Since one of the acids of structure IV has been transformed into a naturally occurring resin acid already and similar partial syntheses of other resin acids seemed assured, a transformation of I-III into IV appeared to lead the way to a stereospecific total synthesis of the most abundant diterpenic natural products. The present communication describes attempts in this direction, and reveals new data on two important points in organic synthesis, the site of alkylation of unsymmetrical ketones and the position of keto–enol equilibrium of cyclic β-ketoesters.

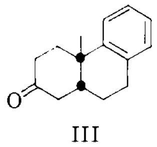


I

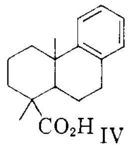


II

a, R = R' = H
b, R = H, R' = CO_2Me
c, R = CO_2Me, R' = H



III



IV

At first a base-catalyzed carbonation of the tricyclic ketone Ia came under consideration. While prior to our study the only alkylations of systems comparable to Ia had led to substitution at C-4,[4] our desired position, it was decided to carry out our reaction under conditions of irreversible enolate anion formation so as to learn more about the mechanistic detail of this first step of the alkylation process. The carbonation therefore was conducted by the interaction of Ia with triphenylmethylsodium, followed by the introduction of dry CO_2 gas and, finally, by reaction with diazomethane.[5] Whereas enolates V and/or VI might lead to three esters, *i.e.*, carbomethoxylation at C-2, 4 and 6, the reaction gave only two crystalline products.

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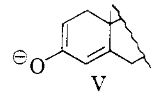
[1] This work was presented at the 16th International Congress of Pure and Applied Chemistry, Paris, France, July 18–24, 1957, and constitutes an excerpt from the Ph.D. dissertation of B. G. J., Iowa State College, June, 1957.

(2) (a) and (b) E. Wenkert and T. E. Stevens, THIS JOURNAL, **78**, 2318, 5627 (1956); (c) E. Wenkert and R. D. Youssefyeh, unpublished data, *cf.* Ph.D. dissertation of R. D. Youssefyeh, Iowa State University, June, 1959.

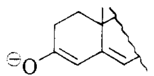
(3) (a) and (b) E. Wenkert and B. G. Jackson, *ibid.*, **80**, 211, 217 (1958); (c) E. Wenkert and J. W. Chamberlin, *ibid.*, **81**, 688 (1959).

(4) (a) R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives and R. B. Kelley, *ibid.*, **76**, 2853 (1954); for a complete description of this work *cf. J. Chem. Soc.*, 1131 (1957); (b) G. Stork and J. W. Schulenberg, THIS JOURNAL, **78**, 250 (1956).

(5) *Cf.* H. M. E. Cardwell, J. W. Cornforth, S. R. Duff, H. Halterman and R. Robinson, *J. Chem. Soc.*, 373 (1953). A similar carbonation had been carried out successfully on cholestenone by T. F. Stevens in this Laboratory.

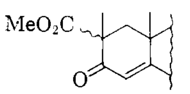


V

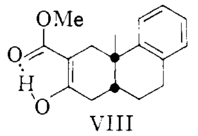


VI

One product could be shown to be Ib on the basis of the data presented. Its ethanolic solution gave an instantaneous strongly positive ferric chloride test. While an analytically pure sample revealed spectral properties of only saturated ester and conjugated unsaturated ketone chromophores, those of its chromatographically pure precursor indicated the presence of its enolic tautomer. Catalytic hydrogenation of Ib yielded a dihydro derivative which was highly enolic. These observations were explicable only on the basis of the presence of the ester group alpha to the ketonic carbonyl function, and hence excluded rigorously a 6-carbomethoxy group from further consideration. The remaining two possible structures, Ib and c. could be differentiated by an inspection of the spectral properties of the product of C-methylation of the ketoester. The non-enolizable product still possessed saturated ester and conjugated enone functions. This implied that the methylated material was VII, and, hence, the carbonation product was a 2-carbomethoxy ketone (Ib), since a compound of structure IIc would have been expected to yield a 4-methyl-Δ^5, and thus unconjugated, substance. The formation of exclusively *cis*-ketone III by acid hydrolysis of the crude reaction mixture from the catalytic hydrogenation of Ib supported formula VIII for its dihydro derivative.



VII



VIII

The second carbonation product was neither enolic nor readily enolizable. Whereas its methylation led to a mixture of unrecognizable products, its catalytic hydrogenation yielded a mixture of ketonic and enolic substances from which a wholly ketonic dihydro derivative could be isolated as the major product. The latter showed no tendency to enolize, but was a β-keto-ester, since it could be hydrolyzed in acid exclusively to *trans*-ketone IIa. When the mother liquor from the crystallization of this ketoester was exposed to a similar acid hydrolysis, both *trans*- and *cis*-ketones IIa and III, respectively, were obtained. This suggested that the minor product, presumably the preponderantly enolic one, belonged to the A/B *cis* series. These results left only structure Ic for the second carbonation product, and, thus, IIc for its dihydro derivative. While the ketonic character of the latter will require further explanation, the slow enolizability of Ic was expected. For ready enolization the olefinic double bond must migrate from the Δ^4- to Δ^5-position, but unfortunately such migration is much slower than its reverse process.[6] Assignment of the equatorial 4α-configuration for the carbomethoxy group in IIc was based on its non-isomerization on treatment with sodium methoxide. The reduction of Ic to IIc could not have been a one-step process, since a normal *cis*-hydrogen addition during the catalytic reduction of the Δ^4-linkage in Ic could have led only to 4-β-substituted *trans* or 4-α-substituted *cis* systems. Most probably the hydrogenation proceeded by 1,4-addition of hydrogen across the enone group, followed by equilibrium-controlled ketonization of the resulting enol of IIc.

In view of the necessity of achieving high yields of IIc for further synthesis the formation of any A/B *cis* compound in the reduction of Ic had to be suppressed. For this reason the *p*H dependence of the stereochemistry of the hydrogenation process was studied and the tricyclic ketone Ia used as a model. Hydrogenation of an ethanolic solution of Ic over palladium–charcoal had been shown already to yield 85–90% of *cis* product III.[2a] A similar reduction in the presence of base now yielded exclusively *cis*-ketone III, while in the presence of acid a 1:1 mixture of *cis* and *trans* products (III and IIc, respectively) resulted. Advantage was taken of this trend toward *trans* product in acid medium. When the ketoester Ic was reduced under similar circumstances, an 80% yield of the desired *trans* product IIc was realized.

The sharp contrast between the production of both 2- and 4-substituted compounds in our rate-controlled carbonation of Ia and the formation of solely 4-substituted products in previous potassium *t*-butoxide-induced alkylations of systems comparable to Ia[4,7] illustrates a fundamental difference in the formation of the intermediate anions V and VI. Exclusive C-4 substitution in the former cases could have occurred only by prior equilibration of V and VI and consequent great accumulation of the more stable heteroannular dienoid system VI. On the other hand, our carbonation results suggest that a kinetically determined proton removal leads to an almost equal distribution of V and VI. This is perhaps somewhat surprising in view of the expected preponderance of V, on the assumption that the more acidic hydrogen at C-2 should have been attacked faster by base than its counterpart at C-6. In fact, the comparable rate of formation of V and VI seems to indicate that the transition state of proton removal by triphenylmethide ion involves a fair amount of bond-breaking and thus resembles the structure of the product. This hypothesis could be tested further by an investigation of the carbonation of the saturated tricyclic ketone IIa. If the transition state of enolate formation depended on the nature of the starting material, the steric and electronic similarity of the α-hydrogens at C-2 and 4 in IIa would lead one to predict comparable rates of production of IX and X, and, thus, comparable yields of XI and IIc. If, however, the transition state is mostly dependent on product stability, IX would be produced more rapidly than X,[8] and, hence, high yields of XI could be predicted. Carbonation of

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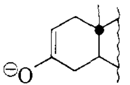
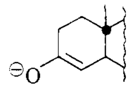
[6] *Cf.* C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 687 (1950).

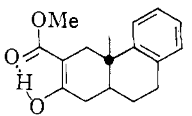
[7] *t*-Butoxide-induced alkylation, especially methylation, of cyclohexenones have become so numerous during the last two years that a citation of all references becomes too cumbersome. Most reported reactions follow the directions of the initial process[1a] and all lead to products analogous to Ic.

[8] *Cf.* R. B. Turner, W. R. Meador and R. E. Winkler, THIS JOURNAL, **79**, 4122 (1957).

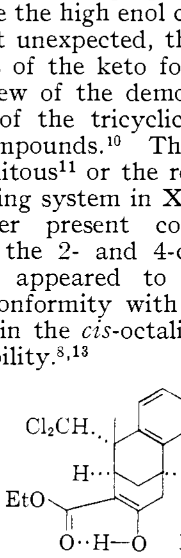
IIa yielded a mixture of products consisting of the new 2-carbomethoxy product in highly enolic form (XI) as well as IIc. The product ratio of XI:IIc was over 7:1.[9]


IX

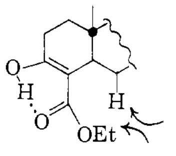

X

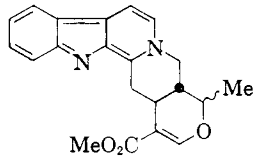

XI

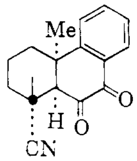
The above transformations had made available three of the four possible saturated β-ketoesters and had yielded some indirect data regarding the fourth. Except for the 4-carbomethoxy A/B *trans* system IIc, all ketoesters were preponderantly enolic in solution. While the high enol content of the latter systems was not unexpected, the presence of even small quantities of the keto forms was somewhat surprising in view of the demonstration of 100% enol character of the tricyclic β-ketoester XII[2b] and similar compounds.[10] This slight difference was either fortuitous[11] or the result of the greater rigidity of the ring system in XII than that in the ketoesters under present consideration.[12] The fact that both the 2- and 4-carbomethoxy A/B *cis* compounds appeared to be predominantly enolic was in conformity with the view that Δ^2- and Δ^3-isomers in the *cis*-octalin series may be of comparable stability.[8,13]


XII

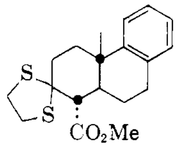
The anomalous lack of enolization of the A/B *trans*-4-carbomethoxy compound IIc, recently again observed in two similar cases,[14] could be ascribed to two factors. Firstly, the Δ^3-*trans* system possesses an energetically unfavorable configuration.[8] Secondly and perhaps more importantly, the enol would be most unstable since the carbomethoxy group would offer strong steric repulsion to the equatorial C-6 hydrogen atom (see arrows in XIII). This *peri effect,* observable in the decalin series only with *trans* compounds or substances possessing double bonds toward a bridgehead, has been responsible for the lack of enolization of XIV[3a] and the lack of coplanarity of the β-alkoxyacrylate moiety of alstonine (XV).[15,16]

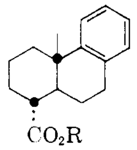

XIII

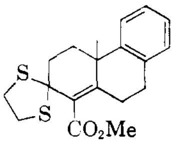

XV

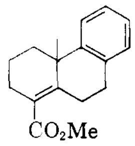

XIV

The saturated ketoester IIc was converted to a thioketal (XVI). Raney nickel desulfurization of the latter yielded a liquid saturated ester (XVIIa), which was characterized by hydrolysis to a crystalline acid (XVIIb). Ketal formation of the unsaturated ketoester Ic led to XVIII, whose desulfurization gave XIX. Both unsaturated esters were Δ^4-compounds as indicated by strong end absorption in the 220 mμ region of their ultraviolet spectra and by 5.82 μ infrared carbonyl bands, as contrasted to the 5.78 μ bands of their saturated analogs XVI and XVIIa. Attempted *t*-butoxide-induced methylation of the esters XVIIa and XIX was unsuccessful. Methylation of the ketoester IIc will be considered in a future communication.


XVI


XVIIa. R = Me
b, R = H


XVIII


XIX

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[9] A further interesting case in conformity with the above hypothesis is the recent tritylsodium-induced methylation of a *cis*-ketone comparable to III at an α-position analogous to our C-4 [E. J. Corey and E. W. Cantrall, THIS JOURNAL, **81**, 1745 (1958)].

[10] O. L. Chapman and J. Meinwald, *J. Org. Chem.*, **23**, 162 (1958).

[11] *Cf.* S. P. Findlay, *ibid.*, **22**, 1385 (1957); **23**, 391 (1958).

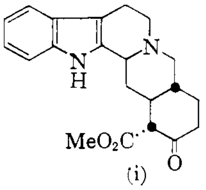
[12] *Cf.* footnote 15 in ref. 2b.

[13] While the hydrogen-chelated enols have been described in every case as endocyclic double-bonded systems, *e.g.*, VIII, the exact nature of the bonds between hydrogen and its surrounding oxygens is not determined. Whereas in principle the chelate may be the enol of the keto group, as in VIII, the enol of the ester group, as recently portrayed by F. M. Dean, T. Francis and K. Manunapichu [*J. Chem. Soc.*, 4551 (1958)], or the symmetrical system, wherein the hydrogen finds itself equidistant from both oxygen atoms, its most acceptable structure at present is the first, *e.g.*, VIII. The electronic configuration of the two functional groups in a β-ketoester is such as to make the preferred enolization of the ester carbonyl group quite unlikely. Furthermore, the dissimilar electron density in the two oxygens available for chelation as well as the lack of symmetry of the over-all system would act against a symmetrical chelate. The steric arguments presented by Dean and co-workers to justify an enolized ester structure are the very ones to favor a shift in the tautomeric equilibrium toward the keto form. Their attempt to draw a parallel between the presumed instability of an endocyclic double bond in their system, and, hence, the presumed instability of chelates equivalent to XII, and the lack of reactivity of certain compounds, expected to form such a double bond, is far from convincing since product stability need not necessarily determine the pathway of a reaction [*cf.* G. S. Hammond, THIS JOURNAL, **77**, 334 (1955)].

[14] P. A. Stadler, A. Nechvatal, A. J. Frey and A. Eschenmoser, *Helv. Chim. Acta*, **40**, 1373 (1957); N. A. Nelson and R. N. Schut, THIS JOURNAL, **80**, 6630 (1958).

[15] N. Neuss and H. E. Boaz, *J. Org. Chem.*, **22**, 1001 (1957).

[16] A further example of the *peri effect* is portrayed by the lack of enolic properties of yohimbinone (i) [A. Le Hir and E. W. Warnhoff, *Compt. rend.*, **246**, 1564 (1958)]. The authors are most grateful to Dr. Warnhoff for a sample of this substance.


(i)

Experimental[17]

Carbonation of Ketones Ia and IIa.—An equimolar quantity of a previously prepared and standardized ether solution of sodium triphenylmethyl was added to a stirred, nitrogen-blanketed solution of 5.00 g. of Ia in 20 ml. of dry ether. Immediately after the addition of the base a stream of dry carbon dioxide gas was bubbled through the suspension for a period of one hour. Thereafter the reaction mixture was decomposed with ice and the organic phase quickly extracted with four 75-ml. portions of ice-cold 5% aqueous sodium hydroxide solution. The combined basic extracts were neutralized rapidly with ice-cold 10% hydrochloric acid and the acid solution immediately extracted with ether. The combined organic extracts were poured into an ether solution of *ca.* 1.5 g. of diazomethane and the mixture allowed to stand for 10 min. The excess diazomethane then was destroyed by washing the ether solution with 10% hydrochloric acid. The organic solution was washed with sodium bicarbonate solution, dried over anhydrous magnesium sulfate and evaporated to dryness, giving 3.96 g. of a yellow gum. The latter was chromatographed over 150 g. of silicic acid–Celite. Elution with 1:1 petroleum ether–benzene gave 75 mg. of triphenylmethane, while elution with 20:1 petroleum ether–ether yielded 1.11 g. of a keto–enol mixture, m.p. 90–107°; infrared spectrum (CCl_4), C=O 5.77(s), 5.97(s), 6.03(s) μ. Three crystallizations from petroleum ether gave colorless prisms of the ketonic form of Ib, m.p. 111–112°; spectra: ultraviolet, λ_{max} 238 mμ (ϵ 18,500); infrared (CCl_4), C=O 5.77(s), 5.97(s) μ; C=C 6.12(m) μ.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.55; H, 6.63.

Elution with 10:1 petroleum ether–ether gave 1.83 g. of another ester, m.p. 116–118°. Two crystallizations from petroleum ether yielded analytically pure ketoester Ic, m.p. 117–118°; spectra: ultraviolet, λ_{max} 239 mμ (ϵ 14,300); infrared (CCl_4), C=O 5.77(s), 5.97(s) μ; C=C 6.15(m) μ.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.70; H, 6.60.

Continued elution with more polar solvents gave 1.07 g. of a yellow-brown gum.

The ether solution of the material, remaining in the ether layer after the initial sodium hydroxide extraction of the carbonated products, was dried over magnesium sulfate, evaporated to dryness and the resulting semi-crystalline gum chromatographed over alumina. The petroleum ether–benzene eluates yielded triphenylmethane, m.p. 79–80°, while elution with 10:1 petroleum ether–ether gave 1.22 g. of starting ketone Ia, m.p. 87–89°, identical m.p., m.m.p. and infrared spectrum with those of an authentic sample.

Identical carbonation of 1.000 g. of the saturated ketone IIa and chromatography of the crude products over 50 g. of silicic acid–Celite led in the 99:1 petroleum ether–ether eluates to 515 mg. of enolized XI, m.p. 75–77°; infrared spectrum (CCl_4), C=O 6.03(s) μ. Several crystallizations from methanol–water gave colorless prisms of XI, m.p. 77–85°; spectra: ultraviolet, λ_{max} 255 mμ (ϵ 13,800); infrared (CCl_4), C=O shoulders at 5.75(w) and 5.83(w) μ, 6.03(s) μ; C=C 6.18(s) μ.

Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 75.24; H, 7.65.

Elution with 10:1 petroleum ether–ether gave 72 mg. of a solid which on several crystallizations from petroleum ether yielded colorless prisms of IIc, m.p. 127–128°; spectra: ultraviolet, λ_{max} 265 (ϵ 525) and 272 mμ (ϵ 465); infrared (CCl_4), C=O 5.77(s), 5.84(s) μ; negative ferric chloride test.

Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.76; H, 7.12.

Chromatography of the uncarbonated residue over alumina afforded 267 mg. of starting ketone IIa from the 10:1 petroleum ether–ether eluates.

Hydrogenation of Ketones I.—A mixture containing 100 mg. of the hydrophenanthrone Ia, 50 mg. of 5% palladium–charcoal, 10 ml. of ethyl acetate and 0.1 ml. of concentrated sulfuric acid was hydrogenated at room temperature and pressure. After 45 min. and a one-molar uptake of hydrogen, gas absorption ceased. The mixture was filtered, washed with 10% sodium bicarbonate solution, extracted with ether and evaporated. The residue was chromatographed over 15 g. of alumina. Elution with petroleum ether gave in the early fractions 32 mg. of the *cis*-ketone III, indicated by the identity of its infrared spectrum with that of an authentic sample,[2a] and 30 mg. of *trans*-ketone IIa, identified in similar fashion, in the later fractions.

A mixture of 200 mg. of Ia, 15 ml. of methanol, 15 mg. of potassium hydroxide and 75 mg. of 5% palladium–charcoal was hydrogenated at atmospheric pressure and room temperature. After cessation of hydrogen uptake the catalyst was filtered, the filtrate neutralized with 10% hydrochloric acid and the solvent removed under vacuum. A chloroform solution of the residue was washed with water, dried over magnesium sulfate and evaporated. The crude product was chromatographed over 5 g. of alumina, affording in the 99:1 petroleum ether–ether eluates 140 mg. (70%) of *cis*-ketone III, as proved by the identity of its infrared spectrum with that of an authentic specimen.

A mixture of 200 mg. of Ib, 75 mg. of 5% palladium–charcoal and 20 ml. of ethanol was hydrogenated at room temperature and atmospheric pressure. After hydrogen uptake had ceased, the catalyst was filtered and the solvent evaporated leading to 200 mg. of a colorless gum. Half of the crude product was removed and saved for the decarboxylation step described below, while the other half was crystallized from methanol–water, giving 76 mg. of a solid, m.p. 88–93°. An alcoholic solution of this substance gave an instantaneous violet color with alcoholic ferric chloride solution. Five further crystallizations from methanol–water yielded colorless fluffy needles of VIII, m.p. 102–103°; spectra: ultraviolet, λ_{max} 256 mμ (ϵ 10,800); infrared (CCl_4), C=O 5.70(w), 5.82(w), 6.03(s) μ; C=C 6.19(s) μ.

Anal. Calcd. for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 75.08; H, 7.11.

A mixture of 200 mg. of Ic, 75 mg. of 5% palladium–charcoal and 20 ml. of ethanol was hydrogenated at room temperature and atmospheric pressure. After cessation of hydrogen absorption the catalyst was filtered and the solvent evaporated. The resulting gum crystallized on trituration with petroleum ether. The solid was dissolved in hot petroleum ether, filtered, the solution concentrated to smaller volume and cooled. This process led to a crop of crystals, m.p. 117–122°; a second crop, m.p. 95–112°; and a third crop, m.p. 95–107°. Their infrared spectra (KBr) revealed the presence of ketoester in all fractions, strong absorption at 5.77 and 5.82 μ, and small amounts of hydrogen-chelated enol in the first crop and large amounts thereof in both later crops, strong absorption at 6.04 and 6.19 μ. Two crystallizations of the material melting at 117–122° from petroleum ether yielded a substance, m.p. 127–128°, identical in all respects with IIc. The combined second and third crops of hydrogenation product and mother liquors from the crystallizations of the first crop were saved for a subsequent hydrolysis.

A mixture of 370 mg. of Ic, 150 mg. of 5% palladium–charcoal, 0.2 ml. of 80% sulfuric acid and 15 ml. of ethyl acetate was hydrogenated at room pressure and temperature. Gas absorption stopped spontaneously after one molar equivalent of hydrogen had been taken up. The catalyst then was filtered, the filtrate washed with 10% sodium bicarbonate solution, dried over magnesium sulfate and evaporated to dryness. Crystallization of the semi-crystalline solid from petroleum ether yielded 295 mg. (79%) of the ketoester IIc, m.p. 126–127°, identical in all respects with an authentic sample.

A sodium methoxide solution (20 mg. of sodium in 20 ml. of anhydrous methanol) of 200 mg. of the ketoester IIc was refluxed for 18 hr. The cooled mixture was poured into 150 ml. of water, acidified with acetic acid and extracted with chloroform. The extract was dried over magnesium sulfate and evaporated. The remaining solid gave a negative ferric chloride test, had an infrared spectrum identical with that of starting material and crystallized from petroleum ether to give crystals, m.p. 126–127°.

Hydrolysis of Ketoesters IIc and VIII.—A mixture of 100 mg. of the crude product from the hydrogenation of Ib, 5 ml. of concentrated hydrochloric acid and 7 ml. of ethanol was refluxed for 18 hr. The cooled acid solution was diluted with 50 ml. of water, saturated with sodium chloride and extracted with chloroform. After drying and solvent evaporation the remaining 75 mg. of yellow gum was chromato-

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[17] Unless otherwise specified, all ultraviolet spectra were taken in 95% ethanol solution on a Beckman DU spectrophotometer. The use of the Baird infrared instrument of the Institute for Atomic Research, Ames, Iowa, herewith is gratefully acknowledged.

graphed over 25 g. of alumina. The petroleum ether eluates yielded 43 mg. of a colorless oil whose infrared spectrum was identical with that of liquid *cis*-ketone III.[2a] None of the further eluates revealed the presence of any *trans*-ketone IIa.

A mixture of 100 mg. of the crude product from the hydrogenation of Ic, 10 ml. of concentrated hydrochloric acid and 10 ml. of methanol was refluxed for 12 hr. The cooled mixture was poured into 25 ml. of water and extracted with chloroform. The extract was washed with 10% sodium bicarbonate solution, dried over magnesium sulfate and the solvent evaporated. The remaining gum, 56 mg., was chromatographed on alumina. The early petroleum ether eluates yielded a colorless oil whose infrared spectrum proved it to be *cis*-ketone III, while the later petroleum ether fractions gave a solid, m.p. 104°, whose infrared spectrum was identical with that of *trans*-ketone IIa.

A mixture of 75 mg. of pure ketoester Ic, 5 ml. of concentrated hydrochloric acid and 7 ml. of ethanol was refluxed for 18 hr. After dilution of the cooled reaction mixture with 50 ml. of water, saturation with sodium chloride and extraction with chloroform, the combined extracts were dried over magnesium sulfate and evaporated to dryness. Crystallization of the slowly crystallizing residue from petroleum ether gave 37 mg. (63%) of a solid, m.p. 98–103°, which on recrystallization from the same solvent proved to be *trans*-ketone IIc, m.p. 107–108°, identical infrared spectrum with that of an authentic sample.[2a]

Methylation of Ib.—A solution of 200 mg. of Ib in 100 ml. of *t*-butyl alcohol was added to a stirred, nitrogen-blanketed solution of 35 mg. of potassium in 100 ml. of *t*-butyl alcohol. After 10 min. of stirring 3.0 ml. of methyl iodide was added. Thereupon the solution was refluxed for three hours, cooled, filtered and the filtrate evaporated to dryness. The residue was taken up in chloroform and water, the chloroform layer separated and the aqueous phase extracted twice with chloroform. The combined extracts were dried over anhydrous magnesium sulfate and evaporated to dryness. Trituration of the crystalline residue with petroleum ether yielded 110 mg. of a solid, m.p. 153–156°, which on four recrystallizations from methanol gave colorless prisms of VII, m.p. 157–158°; spectra: ultraviolet, λ_{max} 239 mμ (ϵ 15,000); infrared (CCl_4), C=O 5.79(s), 5.98(s) μ, C=C 6.12(m) μ.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.89; H, 7.44.

Desoxygenation of the Ketoesters Ic and IIc.—A mixture of 510 mg. of Ic, 0.5 ml. of ethanedithiol, 510 mg. of freshly fused zinc chloride, 1.02 g. of anhydrous sodium sulfate and 20 ml. of anhydrous benzene was stirred at room temperature for 48 hr. The mixture then was taken up in ether and water, the organic layer separated and washed twice with 5% sodium hydroxide solution and once with water. The organic extracts were dried over magnesium sulfate, the solvent evaporated and the resulting yellow gum chromatographed over 15 g. of alumina. Elution with benzene gave 490 mg. (74%) of a solid, m.p. 120–122°, which yielded colorless prisms of thioketal XVIII, m.p. 124.5–125.5°, after three crystallizations from aqueous methanol; spectra: ultraviolet, λ_{max} 272 mμ (ϵ 990), strong end absorption in the 220 mμ region; infrared (CCl_4), C=O 5.82(s) μ.

Anal. Calcd. for $C_{19}H_{22}O_2S_2$: C, 65.88; H, 6.40. Found: C, 66.09; H, 6.26.

A mixture of 490 mg. of XVIII, 1 g. of Raney nickel and 25 ml. of ethanol was refluxed for 12 hr. After filtration of the nickel the solution was evaporated to dryness and the remaining 306 mg. of colorless oil chromatographed on 5 g. of alumina. Petroleum ether elution yielded 244 mg. (68%) of liquid olefinic ester XIX; spectra: ultraviolet, λ_{max} 265 mμ (ϵ 720) and 272 mμ (ϵ 575), strong end absorption in the 220 mμ region; infrared (CCl_4), C=O 5.82(s) μ.

A mixture of 100 mg. of IIc, 0.1 ml. of ethanedithiol, 100 mg. of freshly fused zinc chloride, 200 mg. of anhydrous sodium sulfate and 10 ml. of benzene was stirred at room temperature for 48 hr. The reaction mixture then was filtered, the filtrate washed with 5% sodium hydroxide solution, dried over magnesium sulfate and evaporated. The residue was crystallized from petroleum ether to give 94 mg. of a solid, m.p. 163–166°. Evaporation of the mother liquors, chromatography of the residue over 5 g. of alumina and elution with 10:1 petroleum ether–ether led to an additional 10 mg. of the same solid, m.p. 165–167°. Four crystallizations from petroleum ether yielded colorless prisms of thioketal XVI, m.p. 165.5–166.5°; infrared spectrum (CCl_4), C=O 5.78(s) μ.

Anal. Calcd. for $C_{19}H_{24}O_2S_2$: C, 65.50; H, 6.94. Found: C, 65.18; H, 7.06.

A mixture of 160 mg. of XVI, 2 g. of Raney nickel and 15 ml. of ethanol was refluxed for 10 hr. After filtration of the nickel and evaporation of the solvent under vacuum a petroleum ether solution of the crude product was passed through a short alumina column. Elution with the same solvent yielded 105 mg. (88%) of liquid ester XVIIa; infrared spectrum (CCl_4), C=O 5.78(s) μ.

A mixture of 75 mg. of XVIIa, 10 ml. of 10% sodium hydroxide solution and 10 ml. of ethanol was refluxed for 8 hr. The reaction mixture then was diluted with 100 ml. of water and extracted with chloroform. The aqueous solution was acidified with hydrochloric acid and extracted with chloroform. The latter extract was dried over magnesium sulfate, the solvent evaporated and the crude product crystallized from methanol–water, giving 43 mg. (61%) of solid. Three recrystallizations from aqueous methanol led to colorless needles of the acid XVIIb, m.p. 153–154°; infrared spectrum (CCl_4), OH 2.83(w), 3.30(m) μ and shoulders at 3.07(w) and 3.14(m) μ; C=O 5.75(w), 5.89(s) μ.

Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.71; H, 8.42.

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Photochromic Spiropyrans. I. The Effect of Substituents on the Rate of Ring Closure

BY ELLIOT BERMAN,* RICHARD E. FOX AND FRANCIS D. THOMSON

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The thermal formation of a number of 1,3,3-trimethylindolinobenzopyrylospirans, spiro-(2'H,1'-benzopyran-2,2'-(1,3,3-trimethylindolines)), from their "open form" precursors has been studied spectrophotometrically in ethanol at 6°. The dependence of the rate of ring closure on substituent shows good agreement with the Hammett equation.

Photochromic spiropyrans have been previously investigated notably by Bloch-Chaudé[1] and Hirshberg.[2] These authors have studied both the thermochromic and photochromic phenomena associated with this class of compounds. Our interest in these materials stems from their potential application to chemical systems for data storage.[3]

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