TABLE III

Solvent	Trans-β-Carotene	C-41 Trans-β Carotene	C-42 Trans-β-Carotene	C-46 Trans-β-Carotene
		Solubility, g./100 g.		
Corn oil	0.053	0.064	0.071	0.177
Cottonseed oil	0.060	0.063	0.068	0.210
Olive oil	0.053	0.065	0.069	0.192
Safflower oil	0.049	0.063	0.067	0.175
Glyceryl trioleate	0.059	0.069	0.082	0.224
Preinoleyl alcohol	0.049	0.013	0.023	0.170
Aldol 40	. . .	0.013	0.034	. . .
Aldol 11	0.025	0.033	0.042	0.315
Ethyl laurate	0.180	0.180	0.199	0.250
Ethyl oleate	0.082	0.132	0.161	0.287
Ethyl myristate	0.096	0.174	0.177	. . .
Ethyl acetate	0.057	0.075	0.102	. . .
Propylene glycol	Trace	Trace	Trace	Trace
95% Ethanol	0.0021	0.0019	0.0018	. . .
Aldol 10	0.025	0.033	0.041	0.087
Solubility ratio	1.0	1.2	1.3	3.5

same manner as XIV, there was obtained Xb in yield of 39 g. (61%); m.p. (from ethyl acetate), 154°.

Anal. Calcd. for $C_{46}H_{66}$: C, 89.25; H, 10.75. Found: C, 89.12; H, 10.61.

1,18-Bis(2,6-dimethyl-6-isobutylcyclohexen-1-yl)-3,7,12,16-tetramethyloctadecanonene-1,3,5,7,9,11,13,15,17 (XIb). This compound was prepared in the same manner as XV in yield of 80%, m.p. 164° (from benzene methanol); λ_{max} 457 mμ ($E_{1\,cm}^{1\%}$ 2090); 485–486 mμ ($E_{1\,cm}^{1\%}$ 1650) in cyclohexane.

Anal. Calcd. for $C_{46}H_{68}$: C, 88.96; H, 11.04. Found: C, 88.73; H, 10.61.

Determination of carotenoid solubilities. The relative solubilities for our synthetic homologs and for carotene, in 15 different solvents, were compared. The solubilities were determined by agitating an excess of the crystalline compound with the desired solvent in a 5-cc. screwcap vial sealed under carbon dioxide for 5 days[17] in a rotating shaker (30 r.p.m.). The samples were then centrifuged, and the supernatant liquid was analyzed by ultraviolet spectroscopy. The results are given in Table III.

(17) A. A. Mikhailovinina and B. G. Savinov, *Ukrain. Khim. Zhur.*, **16**, 183–7 (1950).
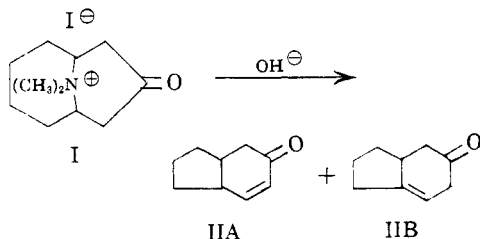
[CONTRIBUTION FROM BAKER LABORATORY, CORNELL UNIVERSITY]

Derivatives of Homopseudopelletierine: Completely Enolic β-Ketoesters

ORVILLE L. CHAPMAN[1] AND JERROLD MEINWALD

Syntheses of the homopseudopelletierine derivatives IIIC, VIIIB, and VIIIC are described. The infrared spectra of these compounds show them to be completely enolized, both in the solid state and in solution. This conclusion is supported by ultraviolet spectral data.

The degradative rearrangement of homopseudopelletierine methiodide (I) in base has been shown to yield the hydrindenone, IIA, along with an iso-


meric product, probably IIB.[2] Three types of mechanism have been suggested to rationalize this transformation.[2] None of these mechanisms could be operative in the case of the dibenzo derivative of I (IIIA), and it was therefore hoped that this compound might give rise to the unrearranged structure IV under elimination conditions. Efforts to prepare IIIA in order to test this reasoning have been unsuccessful and have now been discontinued. We wish, however, to report some incidental findings related to this problem.

The synthesis of compounds of the type III via the Robinson-Schöpf biogenetic technique required

(2) J. Meinwald and M. Koskenkyla, *Chemistry & Industry*, 476 (1955).

III   IV
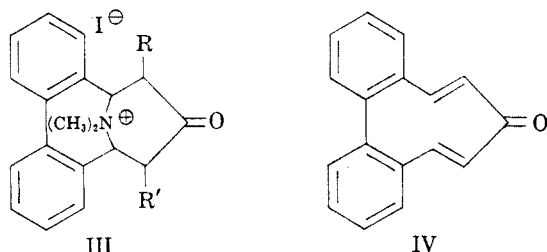
A, R = R' = H
B, R = R' = CO₂C₂H₅
C, R = H; R' = CO₂C₂H₅

a supply of diphenyl-2,2'-d⁼-ldehyde (V). Prior to our work, this aldehyde had been prepared from o-iodobenzaldehyde by treatment with copper powder at high temperatures.[3,4] In the course of this work, we have prepared V via phenanthrene-9,10-quinone (VI) and trans-9,10-dihydrophenanthrene-9,10-diol VII, as shown below.

VIII
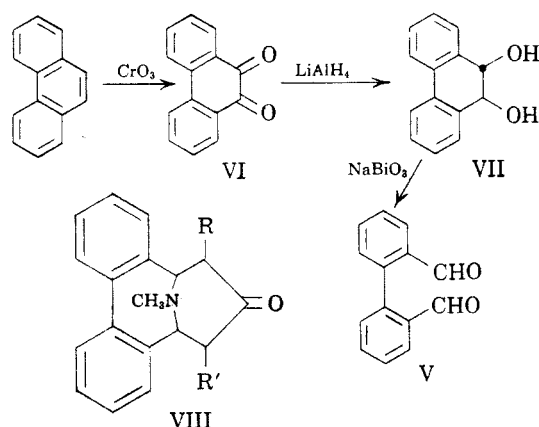
A, R = R' = H
B, R = R' = CO₂C₂H₅
C, R = H; R' = CO₂C₂H₅

Since the development of this method, an even more convenient route to V, consisting of the direct ozonization of phenanthrene, has been described.[5]

The direct condensation of V with acetonedicarboxylic acid and methylamine in aqueous-organic solvent mixtures failed to give VIIIA, probably because of the insolubility of V in the media. The previously described diester VIIIB, however, was readily formed from V using diethyl acetonedicarboxylate and methylamine in ethanol.[3] Attempts to hydrolyze and decarboxylate VIIIB to VIIIA were uniformly unsuccessful. Furthermore, VIIIB itself could not be converted into the methiodide, IIIB, under a variety of conditions. Thus an impasse had been reached at this point.

(3) E. T. L. J. Anet, G. K. Hughes, D. Marmion, and E. Ritchie, Australian J. Sci. Research, Ser. A, 3, 330 (1950).

(4) W. S. Rapson and R. G. Shuttleworth, J. Chem. Soc., 487 (1941).

(5) W. J. Schmitt, E. J. Moriconi and W. F. O'Connor, J. Am. Chem. Soc., 77, 5640 (1955); P. S. Bailey, J. Am. Chem. Soc., 78, 3811 (1956); J. P. Wibaut and T. J. de Boer, Proc. Koninkl. Ned. Akad. Wetenschap. 59, B, 421 (1956).

In the course of studying the properties of VIIIB, it was discovered that treatment with two equivalents of sodium ethoxide in ethanol removed one carbethoxyl group, giving the monoester VIIIC in good yield. The decarbethoxylation of VIIIB is analogous to certain reactions of glutaconic[6] esters and nitromalonic esters.[7]

Attempts to hydrolyze and decarboxylate VIIIC were, however, no more successful than the previously described attempts to carry out these reactions on VIIIB. On the other hand, the monoester VIIIC formed a crystalline methiodide (IIIC) on treatment with methyl iodide. Base degradation of this methiodide gave only an amorphous solid which could not be characterized.

Examination of the infrared spectra of VIIIB, VIIIC, and IIIC led to an unexpected observation. The salient features of these spectra are summarized in Table I. VIIIB shows a band at 5.77–5.78 μ indicative of a normal, isolated ester grouping, while VIIIC is transparent in this region.

TABLE I

INFRARED SPECTRA

|	VIIIB	VIIIC	IIIC
KBr pellet	2.92, 5.77, 6.02, 6.14 μ	2.98, 6.03, 6.20 μ	2.98, 6.03, 6.16 μ
CHCl₃ solution	5.78, 6.01, 6.14 μ	6.04, 6.17 μ	—

The total absence of normal ketonic absorption in the 5.80–5.90 μ region, together with the presence of 6.02 (6.03) μ absorption characteristic of a chelated, conjugated ester carbonyl group[8] and the 6.14 (6.20) μ absorption characteristic of the carbon-carbon double bond in a chelated, enolic β-ketoester[8,9] requires the assignment of the completely enolic structures IX and X to VIIIB and VIIIC, respectively. The case of IIIC is so similar to that of VIIIC that it will not be discussed in detail. This structural assignment is not without analogy. A completely enolic structure has been assigned to diethyl cyclohexanone-2,6-dicarboxylate (XI) on the basis of similar evidence.[8] Ethyl cyclohexanone-2-carboxylate (XII), however, is not completely eno-

(6) F. R. Goss, C. K. Ingold, J. F. Thorpe, J. Chem. Soc., 123, 327 (1923) and references therein cited. The decarbethoxylation of VIIIB requires an excess over one mole of sodium ethoxide. It seems thus that the reaction takes place on the enolate anion. The enol form of VIIIB is actually a glutaconic acid derivative. It is interesting to note that this reaction violates the generalization suggested by Ingold and co-workers that only glutaconic esters which have no mobile hydrogen available for tautomerization will undergo reactions of this type.

(7) C. Ulpiani, Gazz. chim. ital., 35, I, 273 (1905). W. Steinkopf and A. Supan, Ber., 43, 3239 (1910).

(8) N. Leonard, H. S. Gutowsky, W. Middleton, and E. Peterson, J. Am. Chem. Soc., 74, 4070 (1952).

(9) I. M. Hunsberger, R. Ketcham, and H. S. Gutowsky, J. Am. Chem. Soc., 74, 4839 (1952).

IX   X
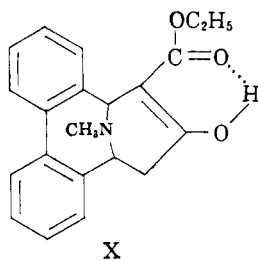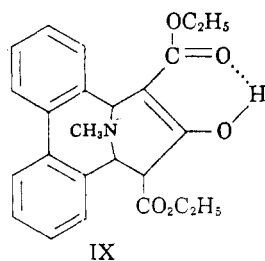
lic.[8] In the polycyclic series, Wenkert and Stevens have called attention to the completely enolic structure required by the infrared spectrum of XIII.[10]

XI

XII

XIII
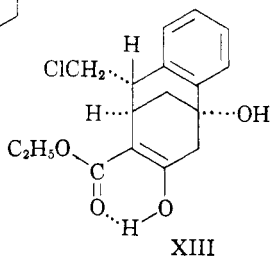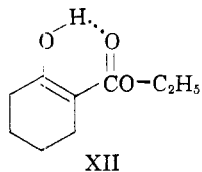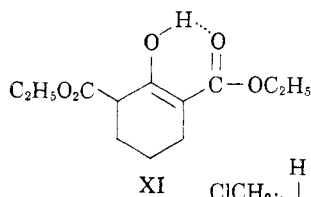
Compounds VIIIB and VIIIC, if enolized would have two chromophores which should absorb in the ultraviolet, the diphenyl system and the enolic β-ketoester. Assuming that there is no interaction between these chromophores, it should be possible to isolate and examine the spectrum of the enolic β-ketoester chromophore by subtracting the spectrum of an appropriate model for the diphenyl system from the spectra of VIIIB and VIIIC. Examination of scale models shows that VIIIB, VIIIC, and XIV have approximately the same conformation of the diphenyl chromophore. Compound XIV was thus selected as a suitable spectral model. The ultraviolet spectra of VIIIB, VIIIC, and XIV are summarized in Table II. The results obtained by

XIV
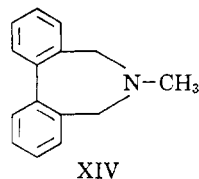
subtracting the spectrum of XIV from the spectra of VIIIB and VIIIC are presented in Table III. The location of the absorption maxima of the resultant spectra is in good agreement with the 245 mμ absorption maximum reported for the enolic form of other β-ketoesters.[11] The ultraviolet spectra

(10) E. Wenkert and T. E. Stevens, J. Am. Chem. Soc., 78, 5627 (1956).

(11) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold Ltd., London, 1954, 223 ff.

of VIIIB and VIIIC thus corroborate the enolic structures IX and X.

TABLE II
Ultraviolet Spectra

	VIIIB	VIIIC	XIV
0.1N H₂SO₄/ 95% EtOH	248 mμ (29,200)	247 mμ (28,700)	248 mμ (16,600)
95% EtOH	248 mμ (29,800)	247 mμ (28,700)	248 mμ (15,500)
0.1N KOH/ 95% EtOH	255 mu (23,700)	255 mμ (23,700)	—

TABLE III
Ultraviolet Subtraction Spectra

	VIIIB–XIV	VIIIC–XIV
0.1N H₂SO₄/95% EtOH	247 mμ (14,300)	245 mμ (12,000)
95% EtOH	248 mμ (13,000)	245 mμ (12,700)

It is difficult to account for the completely enolic structures IX, X, XI, and XIII while remembering that XII and a host of related β-ketoesters are only partially enolic. The difficulty is enhanced by the fact that comparison of scale models of VIIIB and IX or VIIIC and X reveals no steric preference for the enolic or ketonic form in either case. The explanation based on the dipole interactions of the carbonyl groups of a β-ketoester fixed in a rigid polycyclic system suggested by Wenkert and Stevens[10] to account for the enolic structure XIII seems to be the most plausible in the light of the limited data available.

EXPERIMENTAL

Diphenyl-2,2'-dialdehyde (V). Sodium bismuthate[12] (10.0 g.), *trans*-9,10-dihydrophenanthrene-9,10-diol[13] (1.34 g., 0.00632 mole), 10 ml. of 3.33M phosphoric acid, 10 ml. of water, and 10 ml. of dioxane were stirred in a 3-neck flask equipped with a reflux condenser. After approximately 2 min., the reaction mixture became very warm (solvent refluxed). In certain runs, the reaction did not proceed this rapidly; it was then necessary to add 5-ml. portions of 85% phosphoric acid until the reaction proceeded at an appreciable rate. When all the yellow-tan sodium bismuthate had been converted to the white bismuth phosphate, the reaction mixture was stirred for an additional hour. Extraction with ether followed by drying over anhydrous magnesium sulfate and evaporation of the ether gave V as an oil containing some dioxane and any unreacted starting material. The crude product could be used directly for condensations or purified by treatment with sodium bisulfite.

Absolute ethanol (3 ml.) was added to 12 ml. of 40% aqueous sodium bisulfite, and after filtration this solution was added to a solution of the crude product in 2 ml. of absolute ethanol. The resultant cloudy solution was filtered and then extracted with ether. The aqueous-alcoholic solution which contained the soluble bisulfite addition product

(12) For the use of this reagent see W. Rigby, J. Chem. Soc., 1907 (1950).

(13) J. Booth, E. Boland, and E. Turner, J. Chem. Soc., 1188 (1950).

was treated with 15 ml. of concentrated hydrochloric acid and 10 ml. of water. The acid solution was extracted thoroughly with ether. Evaporation of the ether, after washing with water and drying over anhydrous magnesium sulfate, gave V (0.7 g., 52.5%) as a yellow solid, m.p. *ca.* 50°. Recrystallization gave yellow crystals, m.p. 60–62° (reported m.p. 63°).[4]

Diethyl 10-methyl-2,3,4,5-dibenz-10-azabicyclo[4,3,1]deca-2,4-dien-8-one-7,9-dicarboxylate (VIIIB).[3] A solution of V (3.0 g., 0.0143 mole) and diethyl acetonedicarboxylate (3.0 g.) in 20 ml. of absolute ethanol, cooled to 10°, was treated with 1.6 ml. of 30% aqueous methylamine. Overnight, colorless crystals (4.14 g., 71%), m.p. 112–114°, were formed. Recrystallization from methanol gave colorless crystals m.p. 117–118° (reported 118°[3]).

Anal. Calcd. for $C_{24}H_{25}O_5N$: C, 70.76; H, 6.14; N, 3.44. Found: C, 70.54; H, 6.03; N, 3.39.

Attempts to hydrolyze VIIIB *and* VIIIC. A suspension of VIIIB in 5% sodium hydroxide was placed on a shaker for 4–5 hr. The solution was then made acidic with 10% sulfuric acid and refluxed. The time of reflux was varied from 2 to 48 hr. without significant change in the results. The acidic solution was extracted with ether to obtain the neutral and the acidic products. The solution was then made basic and extracted with ether. The only pure product which could be isolated from the mixed neutral and acidic products was a small amount of diphenyl-2,2'-dialdehyde[14] identified by comparison of its infrared spectrum with that of an authentic sample of V as well as by the undepressed mixed melting point of its bis-2,4-dinitrophenylhydrazone with the same derivative of V. The basic products which were obtained (5–20%) constituted a complex mixture from which no pure compound could be isolated.

Similar experiments with VIIIC gave identical results.

Attempts to prepare the methiodide of diethyl 10-methyl-2,3,4,5-dibenz-10-azabicyclo[4,3,1]deca-2,4-dien-8-one-7,9-dicarboxylate (VIIIB). Table IV summarizes the attempts to prepare the methiodide of VIIIB. The reactions were worked up by evaporating the reaction mixture to dryness and recrystallizing the solid thus obtained from ethanol; VIIIB was identified by its melting point and comparison of infrared spectra.

Ethyl 10-methyl-2,3,4,5-dibenz-10-azabicyclo[4,3,1]deca-2,4-dien-8-one-7-carboxylate (VIIIC). A solution of VIIIB (1.0 g., 0.0025 mole) in 50 ml. absolute ethanol was treated with a solution of sodium ethoxide prepared by dissolving 0.12 g. (0.005 mole) of sodium in 10 ml. of absolute ethanol. The solution, under an atmosphere of dry nitrogen, was stirred vigorously with a magnetic stirrer for 2 days. Aqueous hydrobromic acid (10 ml. of 0.5*N*) was added. The solution was diluted with approximately ²/₃ its volume of water and placed in the refrigerator for 11 days. The crystals which had formed were removed by filtration (0.71 g., 82%). These crystals in potassium bromide showed infrared maxima at 2.98, 6.03, and at 6.20 μ but not at 5.77 μ. The prod-

(14) This presumably is produced by the acid-catalyzed reversal of the Mannich condensation.

uct (VIIIC) on recrystallization from methanol formed flat needles which melted at 130–131°; in ethanolic solution it gave a red color with 1% aqueous ferric chloride.

Anal. Calcd. for $C_{21}H_{21}NO_3$: C, 75.23; H, 6.26; N, 4.18. Found: C, 75.40; H, 6.29; N, 3.95.

Ethyl 10-methyl-2,3,4,5-dibenz-10-azabicyclo[4,3,1]deca-2,4-dien-8-one-7-carboxylate methiodide (IIIC). A solution of VIIIC in absolute ethanol was cooled to 0° and then treated with excess methyl iodide. After standing for 2 days, crystals formed. These crystals had an infrared spectrum similar to that of VIIIC but with definite differences. The product was practically insoluble in water; in aqueous-ethanolic solution it gave an immediate precipitate with 5% aqueous silver nitrate. In ethanolic solution it gave an orange-red color with 1% aqueous ferric chloride. After recrystallization from ethanol, the product melted at 186–187°. A mixture melting point with VIIIC was depressed to 159–165°. The methiodide showed infrared maxima (KBr pellet) at 2.98, 6.03, and 6.16 μ.

Anal. Calcd. for $C_{22}H_{24}INO_3$: C, 55.34; H, 5.03; N, 2.94. Found: C, 54.89; H, 5.37; N, 3.09.

Degradation of IIIC. A solution of IIIC (1.0 g.) and sodium carbonate (0.53 g.) in 50 ml. of ethanol-water (1:3) was heated on a steam bath until the presence of dimethylamine could no longer be detected (7–8 hr.). The solution was acidified with 4*N* sulfuric acid and refluxed for a short time. Extraction of the acid solution gave 0.20 g. of a yellow amorphous solid. This material had a complex infrared spectrum with unresolved absorption between 5.77 μ and 6.10 μ. The solid could not be induced to crystallize. The product was converted in poor yield to an orange 2,4-dinitrophenylhydrazone. A chromatogram of this derivative on an alumina column failed to give a pure compound.

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