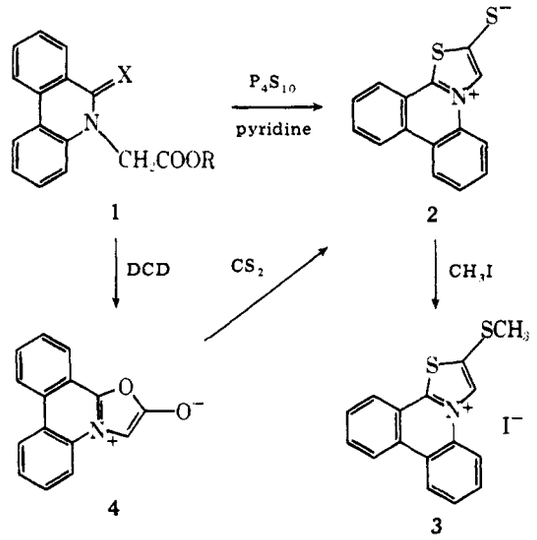
ylcarbodiimide gave the oxazolone 4 which was reacted in situ[5] with carbon disulfide to form 2. This mesoionic system did not undergo cycloaddition with dimethyl acetylenedicarboxylate.

Thionation of the amide carbonyl group is undoubtedly the initial step in the reaction. A longer reaction period converts the acid group into a thio acid which then undergoes a cyclodehydrative ring closure. This is an extremely attractive route



to mesoionic systems of this type but attempts to develop it as a general reaction sequence were unsuccessful under analogous conditions. *N*-Benzoyl-*N*-phenylglycine and its ethyl ester, as well as 2-oxo-1(2*H*)-pyridineacetic acid, gave multicomponent reaction mixtures.

Experimental Section[6]

***anhydro*-2-Mercaptothiazolo[3,2-*f*]phenanthridinium Hydroxide (2). A. By Ring Closure of 1 (R = H; X = O).** 6-Oxo-5(6*H*)-phenanthridineacetic acid[7] (0.5 g, 0.002 mol), P_4S_{10} (0.44 g, 0.002 mol), and pyridine (15 mL) were refluxed for 1 h, the initial light yellow reaction solution turning a deep red after 15 min. After the reaction mixture was poured onto ice, the orange precipitate obtained (0.3 g, 56%) crystallized from DMF or $CHCl_3$–CH_3OH as red plates: mp 298–300 °C dec; UV λ_{max} (C_2H_5OH) 232 nm sh (log ϵ 4.46), 237 (4.48), 252 sh (4.44), 257 (4.46), 263 (4.44), 303 sh (3.93), 310 (3.94), 321 (3.91), 334 sh (3.84), 349 (3.73), 361 (3.71), 392 sh (3.27); IR (Nujol) $\nu_{C=C/C=N}$ 1605, 1555, 1510 cm^{-1}; NMR (TFA) aromatic protons; M^+· *m/e* 267 (100).

Anal. Calcd for $C_{15}H_9NS_2$: C, 67.38; H, 3.39; N, 5.24; S, 23.99. Found: C, 67.16; H, 3.48; N, 5.34; S, 23.44.

B. By Ring Closure of 1 (R = CH_3; X = O). Methyl 6-oxo-5(6*H*)-phenanthridineacetate[7,8] (2.67 g, 0.01 mol), P_4S_{10} (2.45 g, 0.011 mol), and toluene (50 mL) when refluxed for 21.5 h resulted in the formation of a suspension which, after treatment with a solution of $CHCl_3$ (50 mL) and 5% NaOH (50 mL), gave an orange product (2.7 g). Recrystallization gave a product identical[9] with that obtained above.

C. From 1 (R = H; X = O) and DCD/CS_2. The acid 1 (R = H; X = O) (0.64 g, 0.025 mol) and *N*,*N*′-dicyclohexylcarbodiimide (0.60 g, 0.029 mol) were refluxed in CS_2 (30 mL) for 24 h. After cooling, the suspended red product was collected and this product triturated with hot EtOH to remove *N*,*N*-dicyclohexylurea. The orange-red prisms remaining, 0.27 g (40%), mp ca. 300 °C dec, were identical[9] with the product obtained above.

2-Methylthiothiazolo[3,2-*f*]phenanthridinium Iodide[10] (3). A suspension of 2 (0.13 g) in CH_3OH (20 mL) and excess methyl iodide was heated under reflux until a clear yellow solution resulted. The solvent was evaporated and the residue triturated with anhydrous ether resulting in an orange-yellow product (0.18 g) which crystallized from ethanol (Norit) as yellow needles: mp 250–255 °C dec; UV λ_{max} (CH_3OH) 230 nm (log ϵ 4.47), 250 (4.44), 267 (4.62), 293 sh (4.08), 370 (4.14); NMR (Me_2SO-d_6) δ 2.92 (s, 3, SCH_3), 7.67–9.12 (m, 8, aromatic), 9.55 (s, 1, C_5H).

Anal. Calcd for $C_{16}H_{12}NIS_2$: C, 46.95; H, 2.96; N, 3.42. Found: C, 46.90; H, 2.92; N, 3.64.

Methyl 6-Thio-5(6*H*)-phenanthridineacetate (1, R = CH_3; X = S). A mixture of 1 (R = CH_3; X = O), P_4S_{10} (0.566 g, 0.926 mol), and toluene (15 mL) was refluxed for 45 min. After cooling, 5% NaOH (10 mL) and $CHCl_3$ (20 mL) were added and the mixture was stirred for 1.5 h and then filtered. The filtrate was washed with H_2O and saturated NaCl solution, dried ($MgSO_4$), and evaporated. The residue (0.495 g) was chromatographed on silica gel (150 g) using 15% EtOAc–cyclohexane, the product (80 mg, 11%) being collected in 300 mL after a small forerun of eluate. It crystallized from ether as colorless needles: mp 184–185 °C; UV λ_{max} (C_2H_5OH) 245.5 nm (log ϵ 4.61), 250 (4.59), 266 (4.21), 291 (3.92), 308 (3.71), 321 (3.70), 355 sh (3.99), 369 (4.12), 387 (3.99); IR (Nujol) ν_{CO} 1740 cm^{-1}; M^+· *m/e* 283 (100).

Anal. Calcd for $C_{16}H_{13}NO_2S$: C, 67.82; H, 4.62; N, 4.94; S, 11.31. Found: C, 67.99; H, 4.88; N, 4.96; S, 11.22.

Registry No.—1 (R = H; X = O), 37046-34-7; 1 (R = Me; X = O), 62416-28-8; 1 (R = Me; X = S), 62416-29-9; **2**, 62416-30-2; **3**, 62416-31-3; methyl iodide, 74-88-4.

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(5) Several examples of this in situ use of oxazolones have appeared in the literature; e.g., see K. T. Potts and D. McKeough, *J. Am. Chem. Soc.*, **96**, 4268, 4276 (1974); K. T. Potts, J. Baum, E. Houghton, D. N. Roy, and U. P. Singh, *J. Org. Chem.*, **39**, 3619 (1974); F. M. Hershenson, *ibid.*, **37**, 3111 (1972).
(6) Evaporations were carried out under reduced pressure on the steam bath and melting points were determined in capillaries. Spectral characterizations were carried out with the following instrumentation: NMR, Varian A-60A spectrometer; IR, Perkin-Elmer Model 421 spectrophotometer; UV, Cary Model 14 spectrophotometer.
(7) R. F. Cookson, J. W. James, R. E. Rodway, and R. G. Simmonds, *J. Heterocycl. Chem.*, **9**, 475 (1972).
(8) R. M. Acheson and A. O. Plunkett, *J. Chem. Soc.*, 3758 (1962).
(9) Criteria used were superimposable IR spectra and nondepression of mixture melting point.
(10) We thank Dr. J. Baum for this experiment.

A Regiospecific Synthesis of Haematommic Acid

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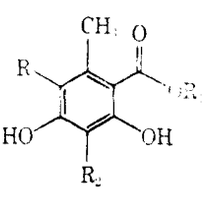
Haematommic acid (**1a**), a common fragment of many depsidones and depsides,[1] has previously been synthesized by two different routes both of which suffer from either experimental difficulties or hazards. St. Pfau[2] first reported the synthesis of **1a** by the reaction of ethyl orsellinate (**1b**) with zinc cyanide and hydrogen chloride in diethyl ether. This reaction yielded a 40/60 mixture of ethyl haematommate (**1c**)

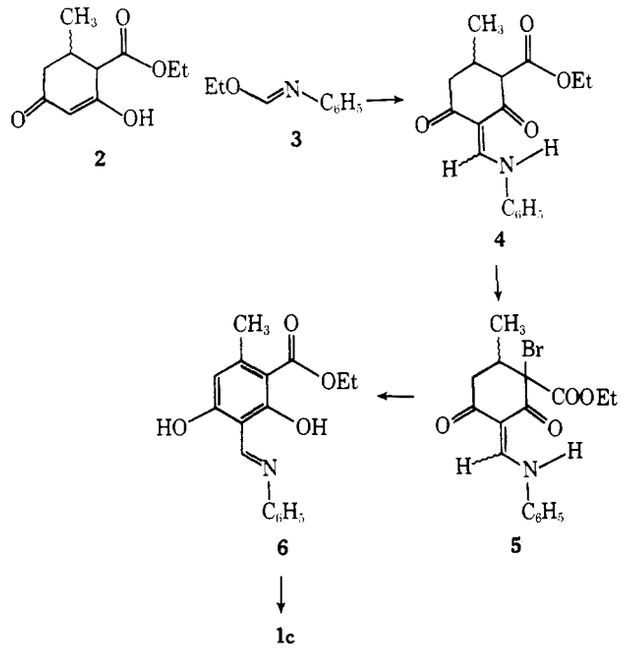


	R_1	R_2	R_3
1a	H	CHO	H
b	Et	H	H
c	Et	CHO	H
d	Et	H	CHO
e	$C_6H_5CH_2$	H	H
f	$C_6H_5CH_2$	CHO	H

and ethyl isohaematommate (**1d**), respectively, which were difficult to separate. Elix[3] has overcome the isomer problem by the reaction of benzyl orsellinate (**1e**) with dichloromethyl methyl ether and titanium tetrachloride. Although this reaction gives specifically benzyl haematommate (**1f**) in 30% yield, the known carcinogenicity of chloromethyl ethers makes this procedure undesirable.

As part of a project directed toward the synthesis of two new depsidones it was necessary to have a convenient synthesis of haematommic acid. Rogers and Smith[4] have shown that cyclohexane-1,3-dione reacts with ethyl *N*-phenylformamidate to yield an anil which can be hydrolized to 2-formylcyclohexane-1,3-dione. Capitalizing upon this reaction we condensed ethyl dihydroorsellinate[5] with ethyl *N*-phenylformamidate[6] (**3**) to yield **4** in 90% yield (Scheme 1). The product

Scheme I



4 was obviously a mixture of two isomers judging from the ^{1}H NMR, which showed two superimposed quartets (J = 7 Hz) centered at δ 4.34 (OCH_2CH_3), two superimposed triplets (J = 7 Hz) centered at δ 1.30 (OCH_2CH_3), and two superimposed doublets (J = 14 Hz) centered at δ 8.72 (C=CHN). The NH hydrogen at δ 13.05 appeared as a broad peak which disappeared upon exchange with D_2O with a corresponding collapse of the two doublets centered at δ 8.72 into two singlets at δ 8.73 and 8.70. Irradiation at δ 13.05 also resulted in the same collapse of the superimposed doublets at δ 8.72. The other features of the ^{1}H NMR were consistent with the proposed structure. It was not determined whether the two isomers were due to the relative stereochemistry of the methyl and carboethoxy groups or to the *E* and *Z* stereochemistry of the enamine double bond since the stereochemistry of both of these positions would be lost upon aromatization of the ring.

A CCl_4 solution of **4** was brominated with *N*-bromosuccinimide in the presence of ultraviolet light to yield **5**. The position of the bromine in **5** was indicated by the absence of the methine (C-1) hydrogen at δ 3.32 in the ^{1}H NMR. As with **4**, the ^{1}H NMR clearly showed a mixture of two isomers. The yield of **5** ranged from 50 to 90% with average in the mid-80%. In the few low-yield cases there was a considerable amount of intractable material produced; however, when the reaction went cleanly the yields were very high.

The dehydrohalogenation of **5** was best accomplished with DBU (1,5-diazabicyclo[5.4.0]undec-5-ene) in Me_2SO/benzene to yield the anil **6** in 51% yield after recrystallization from ethanol. Hydrolysis of **6** to ethyl haematommate (**1c**) in 74% yield was accomplished by stirring an ether solution of **6** with acidic 40% aqueous glyoxal. The physical properties[2] and ^{1}H NMR of the product were consistent with those of ethyl haematommate.

The ester hydrolysis of **1c** by the method of St. Pfau[2] successfully completed the synthesis of haematommic acid.

Experimental Section

Infrared spectra were run on a Beckman Acculab I spectrometer. ^{1}H NMR spectra were run on a Varian T-60 spectrometer using tetramethylsilane as an internal standard. Mass spectra were run on an AEI MS-9 spectrometer at 70 EV. Microanalyses were determined by either Ilse Beetz Microanalytical Laboratory, West Germany, or Galbraith Laboratory, Knoxville, Tenn. Melting points were determined on a Thomas-Kofler micro hot stage and are uncorrected.

Ethyl 6-Methyl-2,4-dioxo-3-[(phenylamino)methylene]-cyclohexanecarboxylate (4). A mixture of 25.5 g (0.131 mol) of ethyl dihydroorsellinate (**2**) and 20.4 g (0.131 mol) of ethyl *N*-phenylformamidate (**3**) was gently heated on a steam bath whereupon an exothermic reaction ensued. Upon cooling the mixture solidified and the crude material was crystallized from 70 mL of boiling ethyl acetate to yield 31.0 g (82%, 0.107 mol) of **4**: mp 121–123 °C; IR 1730 (ester C=O), 1670 (conjugated C=O), 1600 cm^{-1} (conjugated C=C); ^{1}H NMR δ 13.05 (1 H, broad multiplet, NH), 8.72 (1 H, two superimposed doublets, J = 14 Hz, C=CH), 7.4 (5 H, broad multiplet, C_6H_5), 4.34 (2 H, two superimposed quartets, J = 14 Hz, OCH_2CH_3), 3.32 (1 H, two superimposed doublets, J = 5 Hz, CHCOOEt), 3.0–2.0 (3 H, broad multiplet), 1.30 (3 H, triplet, J = 14 Hz, OCH_2CH_3), and 1.10 (3 H, doublet, J = 5 Hz, CH_3); mass spectrum, $C_{17}H_{19}NO_4$, calcd 301.13414, found 301.130537.

Anal. Calcd: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.68; H, 6.32; N, 4.64.

Ethyl 1-Bromo-6-methyl-2,4-dioxo-3-[(phenylamino)methylene]cyclohexanecarboxylate (5). A mixture of 3.01 g (10 mmol) of **4** and 1.85 g (10 mmol) of recrystallized *N*-bromosuccinimide in 150 mL of CCl_4 was stirred at reflux in the presence of UV light for 45 min, during which time the light orange solution turned light yellow and the insoluble material turned to a fine precipitate. The precipitate was filtered and the solvent was removed on a rotary evaporator to yield a crude oil which upon recrystallization from chloroform/cyclohexane yielded 3.10 g (82%, 8.2 mmol) of **5**: mp 150–152 °C; IR 1745 (ester C=O), 1670 (conjugated C=O), 1600 cm^{-1} (conjugated C=C); ^{1}H NMR δ 13.05 (1 H, multiplet, NH), 8.83 (1 H, two superimposed doublets, J = 14 Hz, C=CH), 7.4 (5 H, multiplet, C_6H_5), 4.40 (2 H, two superimposed quartets, J = 8 Hz, OCH_2CH_3), 2.4–3.0 (3 H, broad multiplet), 1.38 (3 H, two superimposed triplets, J = 8 Hz, OCH_2CH_3), and 1.16 (2 H, doublet, J = 5 Hz); mass spectrum $C_{17}H_{18}BrNO_4$, calcd 379.041912, found 379.040515.

Anal. Calcd: C, 53.70; H, 4.77; Br, 21.015; N, 3.684. Found: C, 53.60; H, 4.70; Br, 21.15; N, 3.95.

Ethyl Haematommate Anil (**6**). A mixture of 3.00 g (7.9 mmol) of **5**, 4 mL (48 mmol) of DBU, and 2 mL of Me_2SO in 25 mL of benzene was gently refluxed for 2 h. The dark solution was cooled and poured into 200 mL of water. The aqueous solution was extracted once with a 200-mL portion of ether and twice with 50-mL portions of ether. The combined organic solution was dried over $CaSO_4$ and filtered, and the solvent was removed on a rotary evaporator to yield a crude brown oil. Recrystallization of the oil from 95% ethanol yielded 1.20 g (51%, 4 mmol) of yellow crystals: mp 125–130 °C, IR 3640 (phenolic OH), 1620 (ester C=O), 1590 cm^{-1} (C=N); ^{1}H NMR δ 15.4 (1 H, broad multiplet, phenolic OH), 13.13 (1 H, singlet, phenolic OH), 9.13 (1 H, singlet, N=CH), 7.43 (5 H, singlet, C_6H_5), 6.40 (1 H, singlet, aromatic H), 4.50 (2 H, quartet, J = 8 Hz, OCH_2CH_3), 2.57 (3 H, singlet, aromatic CH_3), and 1.43 (3 H, triplet, J = 8 Hz, OCH_2CH_3); mass spectrum $C_{17}H_{17}NO_4$, calcd 299.1157, found 299.1163.

Anal. Calcd: C, 68.22; H, 5.72; N, 4.68. Found: C, 68.08; H, 5.80; N, 4.44.

Ethyl Haematommate (1c). A mixture of 129.6 mg (0.43 mmol) of **6** was combined with 15 mL of 40% glyoxal, 15 mL of ether, and 4 drops of concentrated H_2SO_4. The mixture was refluxed for 10 h and the layers were separated. The aqueous layer was extracted with six 25-mL portions of ether. The combined ether layer was dried over $CaSO_4$, filtered, and evaporated to yield a crude product which was recrystallized from absolute ethanol to yield 62.2 mg (74%, 0.29 mmol) of **1c**, mp 112–113 °C. The IR and ^{1}H NMR were identical with those

of a sample of ethyl haematommate prepared by the method of St. Pfau.

Acknowledgments. The authors are grateful to Dr. Jon Clardy of Iowa State University and to the Committee for Research and Curriculum Development at the University of Northern Iowa for partial support for this work.

Registry No.—**1a**, 479-25-4; **1b**, 2524-37-0; **2**, 21855-43-6; **3**, 6780-49-0; **4**, 62392-80-7; **5**, 62392-81-8; **6**, 62392-82-9; *N*-bromosuccinimide, 128-08-5.

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Steric Effects. 8. Racemization of Chiral Biphenyls

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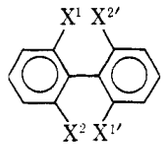
Adams[1] has suggested as a method of predicting the resolvability of chiral biphenyls that when the sum of certain group radii of the groups X^1 and X^2 in I is considerably greater than



I

2.90 Å, the biphenyl will be resolvable; when the sum is considerably less than 2.90 Å, the biphenyl will not be resolvable. We have examined the relationship between the υ steric parameters[2,3] and the Adams group radii. The υ parameters are a function of the van der Waals radii. They are defined by the relationship

$$\upsilon_X = r_{VX} - r_{VH} = r_{VX} - 1.20 \quad (1)$$

where r_{VX} and r_{VH} are the van der Waals radii of the X and H group, respectively. Values of υ were taken from our previous work.[2,3] The group radii used are given in Table I. Correlation was carried out with the equation

$$r_{GX} = m\upsilon_X + c \quad (2)$$

where r_{GX} is the group radius of the X group. Results of the correlation are reported in Table II. The results (set 1) are significant at the 99.9% confidence level (CL). Exclusion of the values for CO_2H and NO_2 (set 1A) results in very much improved correlation as is shown by the value of the F test for significance of the results. Thus, eq 2 has been verified. The deviation of CO_2H and NO_2 is not surprising as the υ values of these groups will be strongly dependent on the transition state of the reaction being studied.

New values of υ were calculated for the NO_2 and CO_2H groups from the appropriate r_{GX} values using set 1A of Table II. They are 0.59 and 0.37, respectively. The value for NO_2 seems reasonable, but the value for CO_2H appears to be too low.

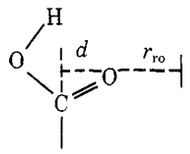
Table I. Data Used in Correlations[a]

1. Adams group radii
H, 0.94; F, 1.39; OH, 1.45; CO_2H, 1.56; NH_2, 1.56; Me, 1.73; Cl, 1.89; NO_2, 1.92, Br, 2.11; I, 2.20
2. Half-lives of 3′-substituted 2-NO_2-6CO_2H-2′-MeO-biphenyls in EtOH at 25 °C
H, 9.4; MeO, 98.1; Me, 332; C, 711; Br, 827; NO_2, 1905
3. Half-lives of 4′-substituted 2-NO_2-6-CO_2H-2′-MeO-biphenyls in MeAc at 25 °C
MeO, 2.6; Me, 3.6; Cl, 12; Br, 25; NO_2, 115
4. Half-lives of 5′-substituted 2-NO_2-CO_2H-2′-MeO-biphenyls in EtOH at 25 °C
H, 9.4; OMe, 10.8; Me, 11.5; Cl, 31; Br, 32; NO_2, 35.4

[a] All data from ref 1 and 6.

These conclusions are based on the point that a planar π-bonded substituent can exist in two extreme conformations with respect to a benzene ring, coplanar or perpendicular. In the perpendicular case, the half-thickness of the substituent determined its υ value, which is minimal and will be referred to as υ_{min}. In the coplanar case the υ value can be calculated as shown in Chart I. It represents a maximal value of υ and is

Chart I



designated υ_{max}. Thus,

$$\upsilon_{max} = d + r_{VO} - 1.20 \quad (3)$$

where r_{VO} is the van der Waals radius of oxygen. Values of υ_{max} and υ_{min} for NO_2 and CO_2H are 1.30, 0.35, and 1.48, 0.50, respectively.

Our results make possible the calculation of Adams group radii from the large number of υ values available, and therefore permit the estimation of optical stability in biphenyls of type I for a wide range of substituents.

We now turn our attention to rates of racemization of substituted biphenyls. Adams and co-workers[1] have measured half-lives for the racemization of 2-NO_2-6-CO_2H-2′-MeO-biphenyls substituted in either the 3′, the 4′, or the 5′ position. These data are reported in Table I. The half-life is related to the rate constants for racemization. The effect of the substituent in the 3′ position has been ascribed to the "buttressing effect". According to Eliel[4] and Ferguson[5] the effect of the substituents in the 4′ position is not well understood. The effect of substituents in the 5′ position is also said to be due to buttressing.[4,5] To investigate these various effects we have examined the correlation of the half-lives by means of the equation

$$\log t_{1/2,X} = \alpha\sigma_{IX} + \beta\sigma_{RX} + \psi\upsilon_X + h \quad (4)$$

in which the σ_I constants[6] and the σ_R constants[6] are measures of the localized (field and/or inductive) and delocalized (resonance) electrical effects. The results of the correlations with eq 4 are given in Table III. The σ_I constants are from our previous work,[6] the σ_R constants were obtained from

$$\sigma_R = \sigma_p - \sigma_I \quad (5)$$

The necessary σ_p constants are from the compilation of McDaniel and Brown.[8] The υ values, as before, are from our collection[2] with the exception of the NO_2 group, for which the