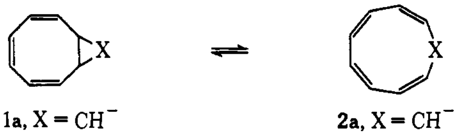
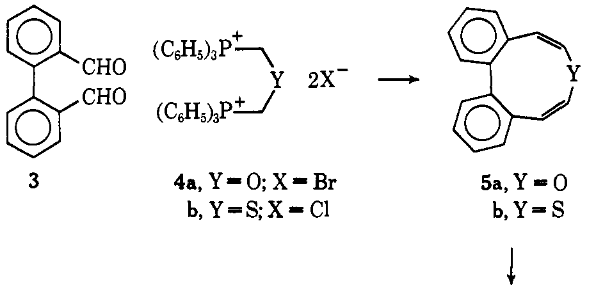
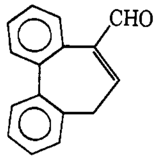


1a, X = CH$^-$ 2a, X = CH$^-$
b, X = O   b, X = O
c, X = S   c, X = S

We now report the synthesis of the first known derivatives of the oxonin and thionin systems, 4,5:6,7-dibenzoxonin (**5a**) and 4,5:6,7-dibenzothionin (**5b**). A Wittig reaction between **3** (1.05 g, 5.0 mmol) and **4a**



3   **4a**, Y = O; X = Br; b, Y = S; X = Cl   **5a**, Y = O; b, Y = S



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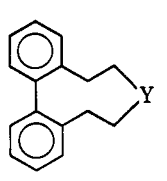

6a, Y = O
b, Y = S

(3.72 g, 5.0 mmol)[9] with lithium methoxide (0.38 g, 10.0 mmol) in DMF at 80° for 3 hr gave, after rapid chromatography on silica gel followed by sublimation, a 6% yield of 4,5:6,7-dibenzoxonin (**5a**), 65 mg, mp 99°. The spectral properties [mass spectrum *m/e* 220.088 (calcd 220.089); ir (CCl$_4$) 1663, 1650 (enol ether double bonds), 1070 cm^{-1} (ether); uv (EtOH) 217 (18,630), 250 (sh) (6285), 293 nm (ϵ 400)] are in accord with the assigned structure.[10] The nmr spectrum, a multiplet at τ 2.2–3.0 (8 H) and an AB double doublet at τ 3.95 (J_{AB} = 7.0 Hz, 2 H) and 4.70 (J_{BA} = 7.0 Hz, 2 H), supports the all-*cis* configuration. Catalytic hydrogenation (Pt, methanol) of **5a** gave 4,5:6,7-dibenzoxonan (**6a**), mp 82–83°, in 80% yield. The mass spectrum (*m/e* 224) showed that four atoms of hydrogen had been added, and the ir and nmr spectra [τ 2.6–3.0 (8 H), 6.0–6.6 (4 H), 7.3–7.7 (4 H)] were in agreement with structure **6a**.

4,5:6,7-Dibenzoxonin (**5a**) behaves as an enol ether, treatment with aqueous hydrochloric acid in ethanol giving an aldehyde [mp 116–117°; uv (EtOH) 227 (24,200), 245 nm (ϵ 22,450)] which was assigned structure **7** on the basis of the mass, ir, and nmr spectral data and by analogy with the behavior of benzo[*d*]oxepin.[9]

A Wittig reaction between **3** (2.1 g, 10.0 mmol) and **4b** (6.60 g, 10.0 mmol)[11] with lithium methoxide (0.146 g, 21 mmol) in methanol under high dilution conditions at room temperature gave, after chromatography on silicic acid, a 10% yield of 4,5:6,7-dibenzothionin (**5b**) (241 mg, mp 121–122°).[12] The spectral properties [mass spectrum, *m/e* 236.065 (calcd 236.066); ir 1615, (vinyl sulfide), 1467, 1437, 1331 cm^{-1}; uv (cyclohexane) 254 nm (sh) (ϵ 5250)] are in accord with the assigned structure. The nmr spectrum, a multiplet at τ 2.6–3.1 (8 H) and an AB double doublet at τ 3.62 (J_{AB} = 10.5 Hz, 2 H) and 4.31 (J_{BA} = 10.5 Hz, 2 H), together with the absence of absorption in the *trans* double bond region of the ir spectrum, supports the all-*cis* configuration. Desulfurization of **5b** with Raney nickel gave the known 2,2′-diethylbiphenyl (71%),[13] and hydrogenation of **5b** (10% Pd–C, EtOAc) for 5 hr gave 38% of 4,5:6,7-dibenzothionan (**6b**), mp 74–75°. The mass spectrum (*m/e* 240.099) showed that four atoms of hydrogen had been added, and the nmr spectrum [τ 2.6–3.1 (8 H), 7.0–7.6 (8 H)] was consistent with **6b**.

The nmr and uv spectra of **5a** and **5b** clearly indicate that these systems are not aromatic and that they exist in buckled, nonplanar conformations. Benzannelation, although it has prevented valence tautomerism to the bicyclo[6.1.0] system, has not led to the adoption of a planar, aromatic conformation.[14] It thus appears that the gain in delocalization energy attained in the planar, all-*cis* conformation is greater for the cyclononatetraenyl anion (**2a**) than for either oxonin (**2b**), 4,5:6,7-dibenzoxonin (**5a**), or 4,5:6,7-dibenzothionin (**5b**).

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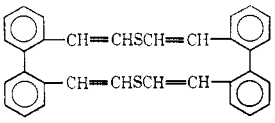
[8] Conversely, annelation depresses cyclic delocalization in the macrocyclic ring system by destabilizing contributing structures involving the disruption of the benzenoid sextet.

[9] K. Dimroth, G. Pohl, and H. Follmann, *Chem. Ber.*, **99**, 634 (1966).

[10] Satisfactory analytical or high-resolution mass spectral data have been obtained for all new compounds.

[11] K. Dimroth, H. Follman, and G. Pohl, *Chem. Ber.*, **99**, 642 (1966).

[12] A second crystalline compound was also isolated (194 mg, 8% yield, mp 125–130°) to which we assign structure i.



i

[13] (a) P. M. Everitt, D. M. Hall, and E. E. Turner, *J. Chem. Soc.*, 2286 (1956); (b) J. R. Shelton and J. F. Suida, *J. Org. Chem.*, **31**, 2028 (1966). The ir spectrum of our sample is in agreement with that reported,[13b] and the mass and nmr spectra are consistent with those expected for 2,2′-diethylbiphenyl. The uv spectrum [230 (4750), 264 (1260), 271 nm (ϵ 910), lit.[13a] *ca.* 227 (sh 6000), 263.4 (730), 271 nm (ϵ 560)] differs from that reported in absorption intensity.

[14] The increase in bond angle strain resulting from annelation may have prevented the adoption of a planar conformation, but this appears unlikely in view of the finding that *sym*-dibenzcyclooctatetraene readily forms the planar dianion.[15] However we are investigating this eventuality by a synthesis of the 1,2:3,4-dibenzocyclononatetraenyl anion.

[15] T. J. Katz, M. Yoshida, and L. C. Siew, *J. Amer. Chem. Soc.*, **87**, 4516 (1965).

A. P. Bindra, J. A. Elix
Chemistry Department, Australian National University
Canberra, ACT 2600, Australia

P. J. Garratt
Chemistry Department, University College
London, W.C.1, England

R. H. Mitchell
University Chemical Laboratories
Cambridge, England

Received October 18, 1968

Rates of Decomposition of Nitro Radical Anions

Sir:

The importance of radical ions as intermediates in organic reactions is now being realized. Heretofore, most investigations have involved aromatic radical ions due to their relative stability and the theoretical insights which arise from their study. We report here some observations on aliphatic radical anions.

Tertiary aliphatic nitro compounds undergo a reversible one-electron reduction to form a radical anion which decays in a first-order fashion to a free radical and nitrite ion.[1] This mechanism is one which

$$RNO_2 \underset{}{\overset{e}{\rightleftharpoons}} [RNO_2]\cdot^- \xrightarrow{k} R\cdot + NO_2^-$$

has been considered by a number of investigators using various electrochemical techniques to determine the first-order rate constant. These techniques have been reviewed recently.[2] We applied the current-reversal chronopotentiometric technique in the manner suggested by Reinmuth and Testa[3] and Dracka.[4]

Nitro compounds were synthesized by the method of Kornblum[5] and purified by sublimation if solid or careful fractionation on a spinning-band column under reduced pressure if liquid. 1-Nitropropane and 2-nitropropane were Eastman Practical Grade materials purified by distillation on a spinning-band column at 100 mm. N,N-Dimethylformamide was purified by the method of Smith.[6]

Chronopotentiometric potential–time curves were recorded on a Tektronix Model 564 storage oscilloscope with Type 3A6 and Type 3B4 plug-ins. Measurements were taken from Polaroid photographs of the traces.

All the nitro compounds investigated showed similar polarographic behavior. One reduction wave was observed at approximately 2.0 V *vs.* a silver perchlorate reference electrode (sre). Triangular wave cyclic voltammetry showed a wave at the expected potential with the oxidation peak height increasing with increasing frequency of scan.

Current-reversal chronopotentiometry was performed on solutions 0.1 *M* in tetra-*n*-propylammonium perchlorate and 1 m*M* in nitro compound in DMF. Forward transition times were always less than 1 sec to minimize spherical error and greater than 5 msec to minimize double layer effects. Transition times were measured using the graphical technique suggested by Reinmuth.[7] The ratio of forward to reverse transition times was calculated and used to obtain respective rate constants from a working curve suggested by Reinmuth and Testa.[3] Table I contains the polarographic half-wave potentials and rate constants measured chronopotentiometrically at ambient temperatures. These results may be compared with a similar investigation[8] using esr at −50°.

The decay of aliphatic nitro radical anions was first viewed as a potential model system for the study of free-radical stability since, due to the strength of the bond being broken, one might expect the transition state to resemble product more than reactant. Insofar as this is true, those factors which stabilize free radicals should also stabilize the transition state. Therefore, the stabilities of the radicals being formed would be reflected by the rate constants for the radical-anion decay. This argument, of course, assumes that the nature of the alkyl group has little effect on radical-anion stability.

Table I. Decomposition of Nitro Radical Anions

Radical anion	$E_{1/2}$[a]	k, sec^{-1} [b]	k, sec^{-1} × 10^2 [c]
1-Nitronorbornyl	1.9[d]	0.39 ± 0.06	1.3
1-Nitroadamantyl	2.05	0.96 ± 0.11	2.6
t-Butylnitro	2.02	1.4 ± 0.1	2.3
Nitrooctyl[e]	2.08	121 ± 15	
2-Nitropropyl	1.9[d]	2.3 ± 0.3	3.5
1-Nitropropyl	1.9[d]	3.5 ± 0.4	5.4

[a] Volts *vs.* sre. The potential of the sre was +0.52 V *vs.* the saturated calomel electrode. [b] Measured chronopotentiometrically at ambient temperature. Values are the result of a minimum of 23 individual measurements in each case. [c] Measured by esr at −50° in DMF. [d] Polarographic maximum. [e] 2,4,4-Trimethyl-2-nitropentyl.

Tertiary nitro compounds which would yield free radicals of widely differing stabilities were synthesized. A chemical investigation[9] has indicated that free radicals exhibit decreasing stability in the series 1-adamantyl > *t*-butyl > 1-norbornyl. If this were reflected in the rate of nitro radical anion cleavage, the size of the rate constant *k* should decrease along the same series. Table I shows that the stability of the incipient free radical must not be the important factor in determining the rate since the size of *k* does not change greatly and decreases in the series *t*-butyl > 1-adamantyl > 1-norbornyl. Thus, the transition state must occur early and resemble reactant more than product. One important factor in determining the rate of radical-anion cleavage is indicated by including the results from a tertiary nitrooctane. The 100-fold acceleration in rate may be due to steric effects since the two radical anions least likely to show steric effects, 1-nitroadamantyl and 1-nitronorbornyl, also show the slowest decomposition rate. A similar acceleration has been observed in carbonium ion reactions and has been explained similarly.[10]

Although the mechanism for reactions of primary and secondary radical anions has not been studied in detail, 1-nitropropyl and 2-nitropropyl radical anions were generated and their disappearance was followed. One reduction wave was observed for both 1- and 2-nitropropanes, as in the case of the tertiary compounds. In addition to the main reoxidation chronopotentiometric wave, however, we observed a second reoxidation wave at about −0.7 V *vs.* sre. This behavior is in contrast to that observed for the tertiary compounds. As the reduction time was shortened (increasing current density), the second wave disappeared, leaving only the main reoxidation wave. At faster times, therefore, the form of the chronopotentiometric waves for 1- and 2-nitropropanes resemble those of the tertiary compounds. Thus, a first-order decomposition under these conditions is postulated. These kinetic results reinforce our contention that the transition state for radical-anion decay occurs early. If one attributes the nitrooctane result principally to a steric effect, the decreasing stability of these radical anions appears to follow the

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(1) A. K. Hoffman, W. G. Hodgson, D. L. Maricle, and W. H. Jura, *J. Am. Chem. Soc.*, **86**, 631 (1964).

(2) W. M. Schwarz and I. Shain, *J. Phys. Chem.*, **69**, 30 (1965).

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(4) O. Dracka, *Collection Czech. Chem. Commun.*, **25**, 338 (1960).

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(6) D. F. Shriver, D. E. Smith, and P. Smith, *ibid.*, **86**, 5153 (1964).

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(9) D. E. Applequist and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 2194 (1965).

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series tertiary > secondary > primary. Since the rate of aliphatic nitro radical anion decomposition seems to reflect the relative stability of radical anions, we shall use this parameter to study such species.

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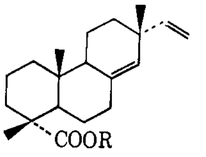
R. H. Gibson, J. C. Crosthwaite
Department of Chemistry
University of North Carolina at Charlotte
Charlotte, North Carolina 28205
Received September 9, 1968

The Synthesis of (−)-Sandaracopimaric Acid

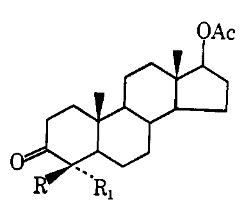
Sir:

We wish to report the synthesis of (−)-sandaracopimaric acid (Ia) from testosterone. This synthesis provides a direct confirmation of the assigned structure and stereochemistry for the natural acid.[1]

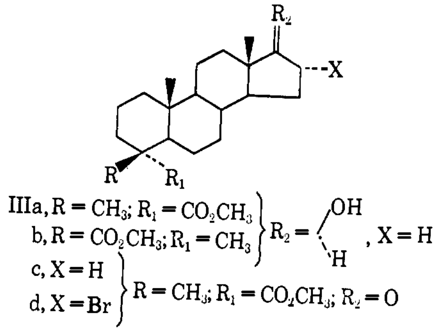


Ia, R = H
b, R = CH_3

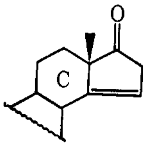
Reductive carbomethoxylation of testosterone acetate using the Stork procedure[2,3] afforded IIa in 24% yield, mp 159–161°, $[\alpha]D$ −2.8°, nmr, δ 3.28 (1 H, doublet, J = 12 cps), 3.76 (3 H, singlet).[4] Methylation[5] of IIa proceeded stereoselectively to afford IIb in 64% yield, mp 166–168°, $[\alpha]D$ −24.1°, and some IIc, mp 200–201°, $[\alpha]D$ −7.3°; the ratio of IIb to IIc formed in this alkylation is 9.2:0.8. Clemmensen reduction of the keto esters IIb and IIc afforded the corresponding 3-deoxy esters[6] IIIa, mp 173–178°, $[\alpha]D$ −6.7°, and IIIb, mp 180–184°, $[\alpha]D$ +37.1°.



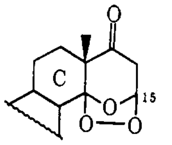
IIa, R = H; R_1 = CO_2CH_3
b, R = CH_3; R_1 = CO_2CH_3
c, R = CO_2CH_3; R_1 = CH_3



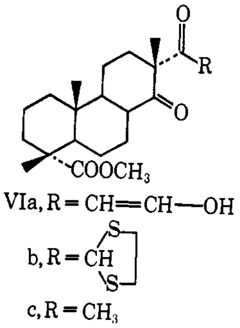
IIIa, R = CH_3; R_1 = CO_2CH_3
b, R = CO_2CH_3; R_1 = CH_3 } R_2 = OH, H, X = H
c, X = H
d, X = Br } R = CH_3; R_1 = CO_2CH_3; R_2 = O



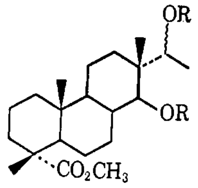
IV



V



VIa, R = CH═CH—OH
b, R = CH(S)(S)
c, R = CH_3



VIIa, R = H
b, R = C_6H_5CO

Oxidation of IIIa with Jones reagent afforded IIIc, mp 140–142°, $[\alpha]D$ +42.9°. Enol acetylation of IIIc followed by bromination[7] afforded the 16α-bromo ketone IIId, mp 220–224°, $[\alpha]D$ +51.9°, which on dehydrobromination with lithium bromide–lithium carbonate in DMF[8] gave the deconjugated ketone IV as the major product, mp 102–103°, $[\alpha]D$ +104.6°. Treatment of IV with ozone at −70° led to the formation of a stable ozonide V, mp 179–185°, in quantitative yield. The protons at C_{15},C_{16} exhibit an ABX splitting pattern in the nmr, $\delta(H_A)$ 2.58, $\delta(H_B)$ 2.86 (2 H, octet, J_{AB} = 17.5, J_{AX} = 1.5, and J_{BX} = 3.0 cps), $\delta(H_X)$ 5.96 (1 H, multiplet, J_{AX+BX} = 5.0 cps). Cleavage of the ozonide by catalytic hydrogenation in the presence of palladized carbon gave the hydroxymethylene ketone VIa, λ_{max}^{MeOH} 259 mμ (ϵ 3000) → $\lambda_{max}^{MeOH-OH^-}$ 296 mμ (ϵ 13,000). Decarbonylation[9] by interacting VIa with ethylene p-toluenethiolsulfonate[10] proceeded smoothly to afford the thioketal VIb, mp 158–161°, $[\alpha]D$ −14.1°, nmr, δ 5.00 (1 H, singlet), 3.35

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[1] (a) O. E. Edwards, A. Nicholson, and M. N. Rodger, *Can. J. Chem.*, 38, 663 (1960); (b) V. Galik, J. Kulhan, and F. Petru, *Chem. Ind.* (London), 722 (1960); (c) A. K. Bose, *ibid.*, 1104 (1960); (d) R. E. Ireland and P. W. Schiess, *J. Org. Chem.*, 28, 6 (1963).

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[4] Satisfactory elemental analyses and spectral data were obtained for all new compounds. Specific rotations were determined on 0.3% solutions in dioxane. Nmr spectra in $CDCl_3$ using TMS as the internal standard were determined on a Varian A-60A spectrometer. The author thanks Mr. M. Yudis and his staff for these physical measurements.

[5] The alkylations were conducted by generating the anion of the keto ester with sodium hydride in refluxing benzene followed by treatment with methyl iodide. A study of the stereochemistry of alkylation of some steroidal keto esters will be included in the full paper.

[6] The stereochemical assignments at C_4 in these compounds were made on the basis of the following evidence. A 3-hr basic hydrolysis at 150° of the equatorial ester IIIa gave a quantitative yield of the corresponding acid, whereas the axial ester IIIb was stable under these conditions. The 19-methyl resonance of IIIb appears at δ 0.70, shielded by 0.19 ppm relative to the corresponding resonance of IIIa at δ 0.89. This 1,3-diaxial shielding effect by a carbonyl group is reported in the tricyclic [E. Wenkert, A. Afonso, P. Beak, R. W. J. Carney, P. W. Jeffs, and J. D. Chesney, *J. Org. Chem.*, 30, 713 (1965)] and bicyclic (*cf.* ref 3) series.

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[10] The author thanks Dr. I. Pachter of Endo Laboratories for a generous gift of this reagent.