us in this manner in high yield (see below). In the camphor synthesis it was presumably formed in the tosylation and/or oxidation step(s) and could be effectively removed by employing the following procedure.[17]

A solution of 790 mg of impure product (consisting of 90% camphor and 10% 2,8-epoxybornane), 863 mg (5.20 mmol) of Girard Reagent T,[9] and 0.80 ml of acetic acid in 8.0 ml of 95% ethanol was heated at reflux for 48 hr. The reaction mixture was cooled, diluted with equal volumes of water and brine, and extracted with pentane.

Purified camphor was recovered by treating the aqueous layer with 1.5 ml of concentrated hydrochloric acid and heating for 2 hr to effect hydrolysis of the Girard derivative. After cooling the camphor was removed by extraction with pentane; the combined pentane extracts were dried, and the solvent was removed under vacuum to yield 513 mg of (±)-camphor of >99% purity as determined by vpc analysis using a 5% SE-30 on Chromosorb W column.

The combined pentane extracts from the initial work-up of the reaction mixture were dried and the solvent was removed under reduced pressure to yield 215 mg of a white solid consisting of 41% camphor and 59% 2,8-epoxybornane (vpc). This mixture was recycled as described above, yielding an additional 108 mg of purified camphor. The combined weights of isolated camphor represent a recovery of 87% of purified product which was sublimed (18 mm, steam bath) to yield a white solid, mp 177–178°. Synthetically prepared (±)-camphor-*8*-^{14}C and (±)-camphor-*9*-^{14}C were both purified in this manner.

2,8-Epoxynorbornane (12).—A solution of 200 mg (0.60 mmol) of 8-tosyloxyisoborneol (7) in 5.0 ml of dry ether was added dropwise to a slurry of 23 mg (0.60 mmol) of lithium aluminum hydride in 6.0 ml of dry ether. The reaction mixture was stirred under nitrogen for 1 hr and then heated at reflux for an additional hour. The mixture was cooled, acidified with 10% sulfuric acid, and extracted with ether. The combined ether extracts were washed with 5% aqueous sodium bicarbonate and dried, and the solvent was removed under reduced pressure to yield 89 mg (95%) of 2,8-epoxynorbornane (12) as a white solid which was sublimed (16 mm, 50°): mp 172–174° (lit.[3] mp 164–167°); the infrared spectrum showed no peaks characteristic of hydroxyl or tosyl groups; mass spectrum (70 eV) *m/e* (rel intensity, fragment ion) 152 (7, M^+), 108 (100, $M^+ - C_2H_4O$ or $- C_3H_8$), 93 (70, 108 − CH_3), 79 (30), 67 (30).

Registry No.—**3,** 29908-22-3; **4,** 29908-23-4; **7,** 29908-24-5; **8,** 29908-25-6; **10,** 21368-68-3.

---

[17] D. J. Pasto and C. R. Johnson, "Organic Structure Determination," Prentice-Hall, Englewood Cliffs, N. J., 1969, p 393.

Addition of Active Methylene and Methine Compounds to 9-Nitroanthracene[1]

Robert H. Williams[2] and H. R. Snyder*

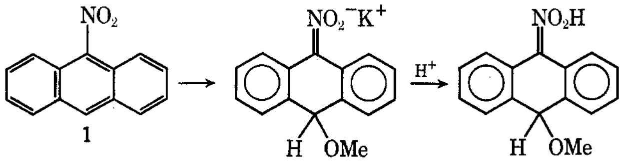
Department of Chemistry, University of Illinois, Urbana, Illinois 61801

Received November 30, 1970

Addition of 9-nitroanthracene to solutions of sodio malonic ester, sodio methylmalonic ester, sodium 2-propanenitronate, and sodio malononitrile in dimethyl sulfoxide and subsequent dilution with water and acidification afford 10-dicarbethoxymethyl-, 10-(1,1-dicarbethoxyethyl)-, 10-(2-nitro-2-propyl)-, and 10-dicyanomethyl-9-nitro-9,10-dihydroanthracenes (**7a–d**), respectively. The results of nmr studies of **7a** are consistent only with the diaxially substituted cis isomer. Addition of benzyl halide to dimethyl sulfoxide solutions of the sodium salts of adducts **7a–c**, followed by aqueous work-up, produces 10-substituted 9-anthrone oximes **10a–c**. Treatment of adducts **7a** and **7b** with acid causes loss of the elements of nitrous acid with the formation of diethyl (9-anthryl)malonate (**12a**) and diethyl methyl(9-anthryl)malonate (**12b**), respectively.

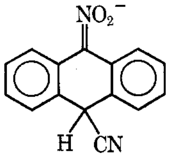
The stable σ complexes formed by nucleophilic attack of certain alkyl nitroaryl ethers by alkoxide ion are known as Jackson–Meisenheimer complexes.[3] These complexes, and structurally similar species, are of theoretical interest because they are possible intermediates in nucleophilic aromatic substitution.[3,4] In some cases the intermediacy of the complex may be shown by spectrometric methods, and some of the complexes are sufficiently stable to permit isolation.[5]

Acidification of Jackson–Meisenheimer complexes (and structurally similar species) normally causes regeneration of the aromatic system; the only exception of which we are aware is reported in the work of Meisenheimer.[6] Complex **2** was prepared by treatment of 9-nitroanthracene (**1**) with methanolic potassium hydroxide. Acidification produced a material for which Meisenheimer suggested structure **3**. It is the purpose of this paper to report the preparation, characterization, and reactions of a series of conjugate acids of anions which structurally resemble Jackson–Meisenheimer complexes.

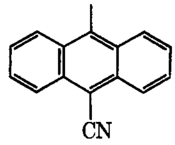


1 **2** **3**

Landolt and Snyder[7] examined the reaction of 9-nitroanthracene with cyanide ion in dimethylformamide. Isolated reaction products included 9-nitro-10-cyanoanthracene (**5a**) and 9,10-dicyanoanthracene (**5b**).



4



5a, X = NO_2
b, X = CN

Dicyanoanthracene **5b** is produced upon treatment of **5a** with cyanide ion under the conditions of the reaction.[7] The mechanism which was proposed for the formation of **5a** involves one-electron transfer from ini-

---

[1] Grateful acknowledgment is made to the U. S. Army Research Office for partial support of this work [Grants DA-ARO(D)-G679 and G857].

[2] NSF Predoctoral Fellow, 1967–1971.

[3] M. J. Strauss, *Chem. Rev.*, **70**, 677 (1970); J. A. Orvik and J. F. Bunnett, *J. Amer. Chem. Soc.*, **92**, 2417 (1970).

[4] (a) E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev. (London)*, **22**, 123 (1968); (b) J. Sauer and R. Huisgen, *Angew. Chem.*, **72**, 294 (1960).

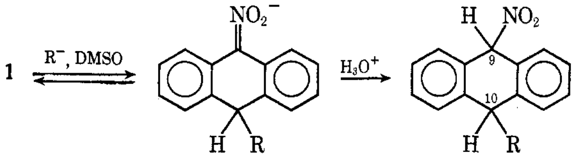
[5] J. H. Fendler, E. J. Fendler, and C. E. Griffin, *J. Org. Chem.*, **34**, 689 (1969); J. H. Fendler, E. J. Fendler, W. E. Byrne, and C. E. Griffin, *ibid.*, **33**, 977 (1968); R. Foster and C. A. Fyfe, *Rev. Pure Appl. Chem.*, **16**, 61 (1966).

[6] J. Meisenheimer, *Ann. Chem.*, **323**, 205 (1902).

[7] R. G. Landolt and H. R. Snyder, *J. Org. Chem.*, **33**, 403 (1968).

tially formed anion **4** and subsequent oxidation of the resulting radical. The overall result of the reaction is the replacement of an aromatic hydrogen atom by a cyano group. The possibility of extending this reaction to other nucleophiles prompted this study.

Adducts.—Addition of 9-nitroanthracene (**1**) to a solution of sodio malonic ester in dimethyl sulfoxide (DMSO) produces an intensely colored solution. Aqueous work-up affords 9-nitro-10-dicarbethoxymethyl-9,10-dihydroanthracene (**7a**) in 68% yield. Analogously, reaction with the anions of diethyl methylmalonate, 2-nitropropane, and malononitrile provides 9-nitro-10-(1,1-dicarbethoxyethyl)-9,10-dihydroanthracene (**7b**, 75%), 9-nitro-10-(2-nitro-2-propyl)-9,10-dihydroanthracene (**7c**, 76%), and 9-nitro-10-dicyanomethyl-9,10-dihydroanthracene (**7d**, 70%), respectively. Dilution of the reaction mixture with water followed by acidification causes precipitation of the crude product as a light yellow solid. The yellow color is removed by recrystallization; the use of 2 equiv of nucleophile in the reactions facilitates purification by reducing the amount of unreacted nitroanthracene.



6a, R = $CH(CO_2Et)_2$
b, R = $CMe(CO_2Et)_2$
c, R = CMe_2NO_2
d, R = $CH(CN)_2$

7a, R = $CH(CO_2Et)_2$
b, R = $CMe(CO_2Et)_2$
c, R = CMe_2NO_2
d, R = $CH(CN)_2$

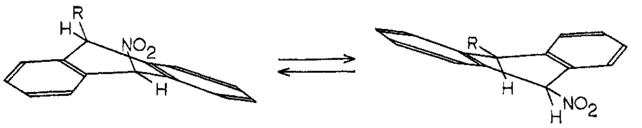
The ir spectra of the adducts contain, in addition to peaks characteristic of R, peaks of medium to strong intensity at *ca.* 1550 and 1360 (NO_2), 750 (ortho disubstituted benzene), and 1450 cm^{-1}. The nmr spectra of the adducts are summarized in Table I. Chemical shift is strongly dependent upon solvent: the AB system of **7d** collapses to a singlet (4.66 ppm) when $CDCl_3$ is used as the solvent. As shown in Figure 1, the $CH(CO_2Et)_2$ doublet is superimposed upon the methylene proton multiplet in the nmr spectrum of a solution of **7a** in acetone-d_6, but, upon change of solvent to C_6D_6, the resonances no longer overlap. Potential magnetic nonequivalence[8] of the methylene protons of **7a**, unlike that of **7b**, is manifest. Analysis of the 220-MHz spectrum[9] of **7a** indicates that the multiplet observed at 3.9 ppm in the 60-MHz spectrum consists of a doublet (J = 10.0 Hz) centered at 3.85 ppm superimposed upon an AB system of quartets centered at 3.96 ppm. Parameters of the AB system are J_{AB} = 10.0 Hz, $\Delta\delta$ = 0.089 ppm, J_{HMe} = 7.0 Hz.

The central ring of the dihydroanthracene system is constrained to the boat form by the two fused benzene rings. A cis diaxially substituted isomer (**8**), a cis diequatorially substituted isomer (**9**), and two trans disubstituted isomers are possible. In addition, the two cis isomers are interconvertible by a boat–boat ring inversion, as are the two trans isomers. Nmr studies of 9-alkyl- and 9,10-dialkyl-9,10-dihydroanthracenes indicate that the equatorial position is more crowded than the axial position, presumably because of steric interaction of the equatorial substituent and the peri protons.[10] Temperature invariance of the nmr spectrum of 9-isopropyl-9,10-dihydroanthracene from 37 to −37° led Brinkmann, *et al.*,[10a] to conclude that the compound is conformationally homogeneous within this temperature range, and only the axially substituted conformer is consistent with the nuclear Overhauser enhancements which they observed. The resonance signals assigned to the benzylic protons of adduct **7a** do not change significantly when the temperature of an acetone-d_6 solution is decreased from 42 to −95°. Temperature invariance of the nmr spectrum indicates either that the adduct is not a rapidly equilibrating mixture of inversional isomers below 42° or that equilibrium is rapid at −95°, which is unlikely.[10a,11a]

Table I
60-MHz Nmr Spectra of Adducts and Oximes[a]

Compd	δ[b]	Multiplicity[c] (J, Hz)	Proton assignment
7a	1.0	t (7)	CH_2CH_3
	3.9	m	CH_2CH_3 + $CH(CO_2Et)_2$
	4.9	d (10) b	H-10
	6.9	s b	H-9
	~7.5	m	Aromatic
7b	0.9	s	$C(CH_3)(CO_2Et)_2$
	1.2	t (7)	CH_2CH_3
	4.1	q (7)	CH_2CH_3
	5.4	s b	H-10
	6.7	s b	H-9
	~7.5	m	Aromatic
7c[d]	1.3	s	CH_3
	4.9	s b	H-10
	6.4	s b	H-9
	~7.5	m	Aromatic
7d	4.9	AB (10.8) ($\Delta\delta$ = 0.106 ppm)[e]	$CHCH(CN)_2$
	7.2	s b	H-9
	~7.8	m	Aromatic
10a	1.0	t (7)	CH_2CH_3
	3.4	d (10)	$CH(CO_2Et)_2$
	4.0	q (7)	CH_2CH_3
	4.8	d (10)	H-10
	7.3–8.5[f]	m	Aromatic
	10.9	s b	NOH
10b	1.1[g]	s	$C(CH_3)(CO_2Et)_2$
	1.2	t (7)	CH_2CH_3
	4.2	q (7)	CH_2CH_3
	5.3	s b	H-10
	7.5–8.6[f]	m	Aromatic
	10.8	s b	NOH

[a] Solvent is acetone-d_6 unless otherwise specified. [b] In parts per million downfield from TMS. [b] Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; b, broad. [d] In $CDCl_3$ solution. [e] The upfield half is due to $CH(CN)_2$. [f] See text. [g] Superimposed upon triplet in 60-MHz spectra.



8 **9**

---

(8) M. van Gorkom and G. E. Hall, *Quart. Rev. (London)*, **22**, 14 (1968).

(9) We gratefully acknowledge a grant to the Department of Chemistry and Chemical Engineering of the University of Illinois from the National Science Foundation, which helped to make purchase of the HR 220 possible.

(10) (a) A. W. Brinkmann, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **92**, 5912 (1970); (b) R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *ibid.*, **91**, 4535 (1969); J. E. Anderson, *Quart. Rev. (London)*, **19**, 426 (1966).

(11) (a) P. T. Lansbury, *Accounts Chem. Res.*, **2**, 210 (1969); (b) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

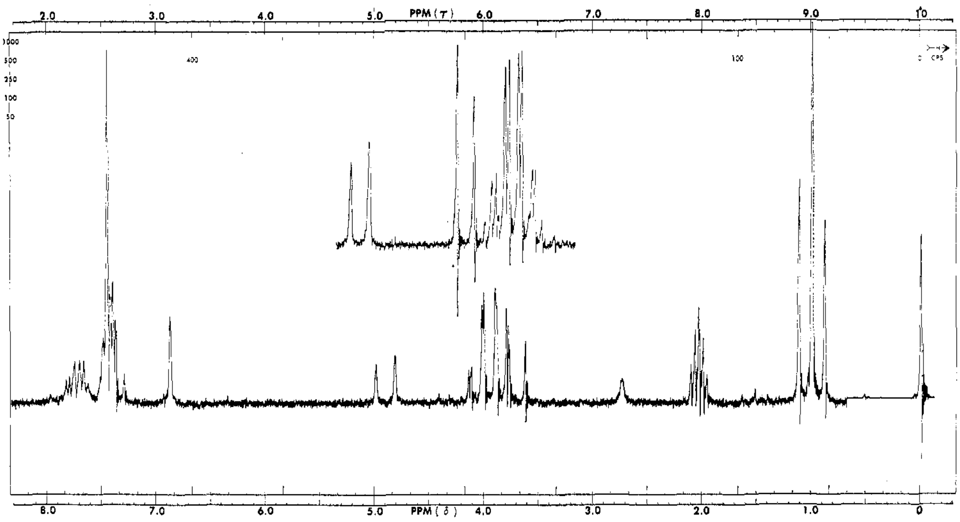


Figure 1.—The 60-MHz nmr spectrum of 9-nitro-10-dicarbethoxymethyl-9,10-dihydroanthracene (**7a**) in acetone-d_6 (lower trace) and in C_6D_6 (upper trace). Solvent impurities (acetone-d_5 and HDO) are responsible for resonances at 2.05 and 2.8 ppm.

Resonance signals arising from benzylic protons of the adducts are broadened by long-range benzylic coupling with ortho and para ring protons. The magnitude of the benzylic coupling constant is dependent upon the dihedral angle between the ring plane and the plane defined by the Ar–C–H bonds; a larger coupling constant should be observed for an axial than for an equatorial proton.[11] In addition, the appearance of these resonance signals will be altered by coupling between the benzylic protons. The magnitude of the homoallylic coupling constant is dependent upon the positions occupied by the benzylic protons; typical values of the homoallylic coupling constant for the dihydroanthracene system are $J_{a,a}$ = 2.5 Hz, $J_{a,e}$ = 1.5 Hz, and $J_{e,e}$ = 0.5 Hz.[10a,12]

Resonance of the C-9 proton of adduct **7a** (C_6D_6 solution) gives rise to a singlet at 6.10 ppm (width at half-height, 1.4 Hz), and resonance of the C-10 proton gives rise to a doublet (J = 10 Hz) centered at 5.17 ppm (width of each peak at half-height, 1.4 Hz). Observed line widths of the benzylic resonances preclude the diequatorially substituted isomer, and consideration of a trans isomer would require an atypically small homoallylic coupling constant. In addition, line widths of the two benzylic resonances of a trans isomer would differ as a result of distinct benzylic coupling constants for axial and equatorial protons.

The resonances of equatorial, but not axial, benzylic protons of dihydroanthracenes are enhanced upon irradiation of aryl resonance signals[10a] (nuclear Overhauser effect[13]). Irradiation of a deoxygenated solution of **7a** in C_6D_6 at 7.50 ppm causes an enhancement of the C-10 proton resonance of 15%, and irradiation at 7.10 ppm causes an enhancement of the C-9 proton resonance of 10%. These data are consistent only with the diaxially substituted cis isomer.

Complex formation proceeds poorly in conventional protic solvents; only nitroanthracene was recovered from an attempted preparation of **7a** in ethanol. Reaction fails to occur in DMSO when a catalytic quantity of base is used, and at least 67% of a sample of adduct **7d** reverted to nitroanthracene upon standing for 2 hr at room temperature in DMSO containing a catalytic amount of dimsyl ion. Reversal of adduct formation also takes place upon dissolution of **7d** in pyridine.

Two factors contribute to the increased rate of nucleophilic substitution reactions in dipolar aprotic media: enhanched reactivity of nucleophile and greater stabilization of the transition state. Haberfield, Clayman, and Cooper[14] have reported that the change in enthalpy of solvation of the nucleophile, on going from polar protic to dipolar aprotic solvent, is not always the primary factor in determining the much smaller activation enthalpies of S_N2 and S_NAr reactions in dipolar aprotic solvents.

Grunwald and Price[15] have emphasized the importance of the contribution to solvation energy made by the dispersion interaction. The dispersion interaction is particularly strong when both solvent and solute are highly polarizable, and its contribution to solvation energy may be dominant. The intense color observed upon treatment of nitroaromatic compounds with base has been ascribed to species similar to Jackson–Meisenheimer complexes[4a,5] and is an indication of the high polarizability expected for a highly delocalized anion (represented in structure **6** by only one of the many limiting resonance forms).

Although the adducts are thermodynamically less stable than the compounds from which they are prepared, the conjugate bases of the adducts are stable in the highly polarizable, dipolar aprotic solvents. Anionic character of the aromatic system, which develops in the transition state and is realized in the complex, increases the strength of the dispersion interaction, and, consequently, the energy of solvation.

Upon protonation of the anion of 9-nitrofluorene, Kerber and Hodos[16] obtained a nitronic acid which is stable in hydroxylic solvents but tautomerizes to 9-nitrofluorene in nonpolar solvents. Protonation of complex **6** may proceed through a nitronic acid (*vide infra*),

---

[12] Note that $J_{e,e}$ is the coupling constant between two equatorial protons and that it is this coupling constant that is expected for a *diaxially* substituted dihydroanthracene.

[13] A. Carrington and A. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, p 229.

[14] P. Haberfield, L. Clayman, and J. S. Cooper, *J. Amer. Chem. Soc.*, **91**, 787 (1969).

[15] E. Grunwald and E. Price, *ibid.*, **86**, 4517 (1964).

[16] R. C. Kerber and M. Hodos, *J. Org. Chem.*, **33**, 1169 (1968).

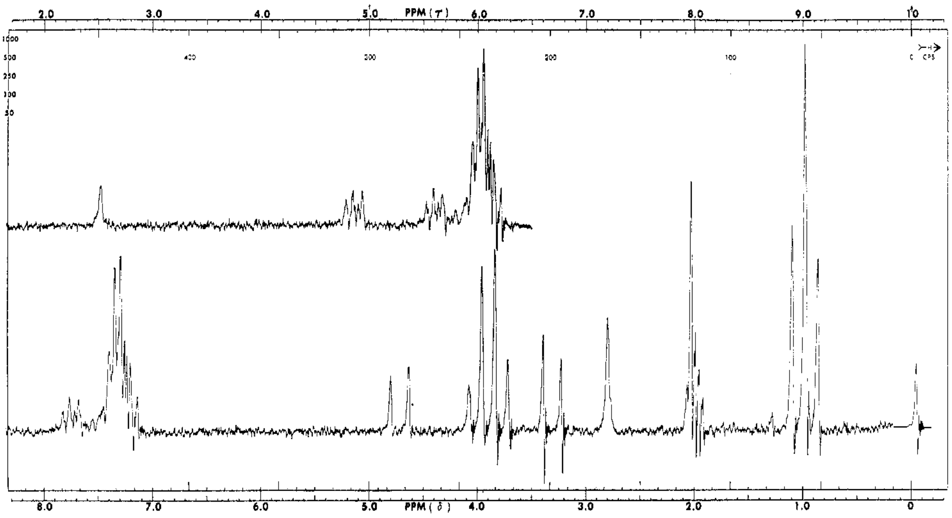
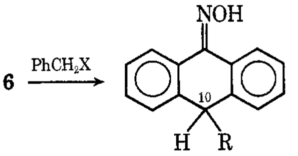


Figure 2.—The 60-MHz nmr spectrum of 10-dicarbethoxymethyl-9,10-dihydro-9-oximinoanthracene (**10a**) in acetone-d_6; upper trace, offset 200 Hz. Solvent impurities (acetone-d_5 and HDO) are responsible for resonances at 2.05 and 2.8 ppm.

but spectral data clearly establish that the adducts isolated are nitro compounds.

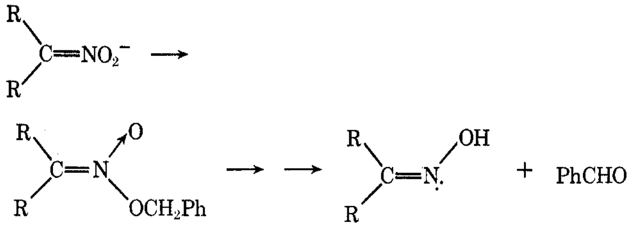
Oximes.—Treatment of solutions of **6a**, **6b**, and **6c** in DMSO with benzyl halide, followed by aqueous work-up, affords 10-dicarbethoxymethyl-9,10-dihydro-9-oximinoanthracene (**10a**, 63%), 10-(1,1-dicarbethoxyethyl)-9,10-dihydro-9-oximinoanthracene (**10b**, 68.5%), and 10-(2-nitro-2-propyl)-9,10-dihydro-9-oximinoanthracene (**10c**, 59%), respectively. Attempted preparation of oxime **10d** by this procedure failed; addition of benzyl chloride to a DMSO solution of **6d** evidently reversed complex formation, for only nitroanthracene was isolated. Some reversion may also have occurred in the preparation of **10b**, since 26% of the nitroanthracene used to prepare the solution of **6b** was recovered upon recrystallization of the crude oxime. Substantial quantities of nitroanthracene are not encountered in the preparation of the adducts (**7a**–**d**) or the other oximes (**10a** and **10c**).



10a, R = $CH(CO_2Et)_2$
b, R = $CMe(CO_2Et)_2$
c, R = CMe_2NO_2
d, R = $CH(CN)_2$

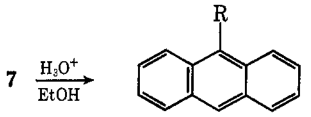
The ir spectra of the oximes contain, in addition to peaks characteristic of R, peaks of medium to strong intensity at *ca.* 1000, 935, and 785 cm^{-1}. The nmr spectra of **10a** and **10b** are summarized in Table I. Because of the low solubility of **10c**, nmr data have not been obtained. Nonequivalence of the methylene protons is not observed for either **10a** or **10b**. Multiplets assigned to aromatic protons of **10a** appear at 8.5 (1 H), 7.8 (1 H), and 7.3 ppm (6 H) (see Figure 2); similarly, multiplets appear at 8.6 (1 H) and 7.5 ppm (7 H) in the spectrum of **10b**.

The mechanism of oxime formation involves base-catalyzed decomposition of the initially formed benzyl nitronate (**11**).[17] Kerber and Hodos[16] have reported that protonation and benzoylation of the anion of 9-nitrofluorene form the nitronic acid and *O*-benzoyl derivative, respectively. Since oxime formation from **6** (which proceeds through an O-alkylated derivative) is observed, it seems likely that protonation initially occurs at an oxygen atom. C-Alkylation of 2-propanenitronate by 9-nitroanthracene occurs in preference to O-alkylation. Thermodynamic, rather than kinetic, factors may be significant here.



11

Reaction of Adducts with Acid.—Exposure to boiling aqueous ethanolic HCl converts **7a** to 9-(dicarbethoxymethyl)anthracene (**12a**) in 93% yield. Analogously, 9-(1,1-dicarbethoxyethyl)anthracene (**12b**) is available from **7b**. Attempted preparation of 9-(2-nitro-2-propyl)anthracene from **7c** failed; the products obtained were oxime **10c** and the corresponding ketone, 10-(2-nitro-2-propyl)-9,10-dihydro-9-oxoanthracene (**13**). The identity of **12a** was confirmed by hydrolysis and decarboxylation to the known[18] (9-anthryl)acetic acid. The identity of **13** was confirmed by conversion to **10c** (95% yield) upon treatment with hydroxylamine hydrochloride in pyridine.



12a, R = $CH(CO_2Et)_2$
b, R = $CMe(CO_2Et)_2$

---

[17] N. Kornblum and R. A. Brown, *J. Amer. Chem. Soc.*, **86**, 2681 (1964).

[18] N. Acton and E. Berliner, *ibid.*, **86**, 3312 (1964).

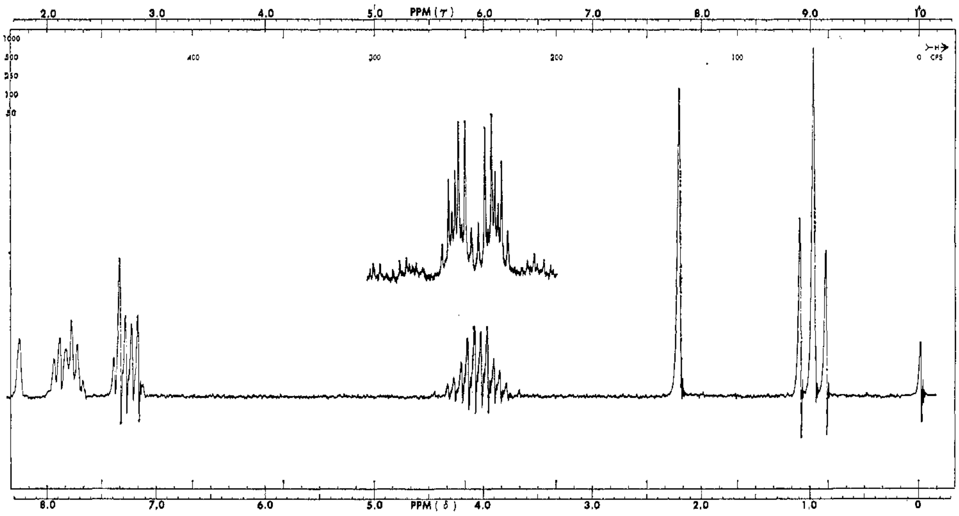
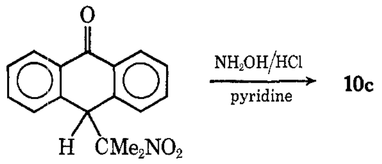


Figure 3.—The 60-MHz spectrum of 9-(1,1-dicarbethoxyethyl)anthracene (**12b**) in CCl_4 (lower trace) and 220-MHz partial spectrum of the methylene proton region (upper trace).



13

As may be seen from Figure 3, the 60-MHz nmr spectrum of **12b** contains a complex multiplet (arising from resonance of nonequivalent methylene protons) at 4 ppm, which is resolved at 220 MHz into an AB system of quartets.[9] The parameters are $J_{AB} = 11$ Hz, $\Delta\delta = 0.12$ ppm, $J_{HMe} = 7$ Hz. The methylene protons of adducts **7a** and **7b**, oximes **10a** and **10b**, and substituted anthracenes **12a** and **12b** are potentially magnetically nonequivalent. The nonequivalence is manifest for **7a**, though not for **10a** or **12a**, and for **12b**, though not for **7b** or **10b**.

Mass spectra have been recorded for each of the new compounds reported, and in each case a fragmentation scheme has been proposed[19] which is consistent with the mass spectral data and which supports the structural assignment. The compositions of key fragments were confirmed by exact mass measurements.[20]

Experimental Section[21]

9-Nitro-10-dicarbethoxymethyl-9,10-dihydroanthracene (7a).—A solution of sodio malonic ester was prepared by stirring diethyl malonate (36 mmol, 5.5 ml) with sodium hydride (36 mmol) in DMSO (50 ml) for 1 hr. To the resulting solution was added a solution of 9-nitroanthracene (18 mmol, 4.02 g) in warm DMSO (75 ml). Stirring was continued for 1 hr, the reaction mixture was poured into 300 ml of water, and concentrated hydrochloric acid was added to reduce the pH to *ca.* 3. The precipitate was collected by filtration and dissolved in 150 ml of 50:50 CH_2Cl_2–ethanol. After treatment with activated charcoal, the solution was concentrated to 50 ml. Upon standing at −15°, the solution deposited 4.76 g (68%) of off-white crystals. Recrystallization from CH_2Cl_2–hexane gave **7a** as white crystals: mp 123.5–124.5°; ir 1745, 1550, 1310, 1260, 1143, 760 cm^{-1}; mass spectrum *m/e* (*I*)[22] 351 (47), 263 (47), 233 (60), 191 (60), 178.0784 (100, $C_{14}H_{10}$), 176 (47).

Anal. Calcd for $C_{21}H_{21}NO_6$: C, 65.79; H, 5.52; N, 3.65. Found: C, 65.72; H, 5.44; N, 3.60.

9-Nitro-10-(1,1-dicarbethoxyethyl)-9,10-dihydroanthracene (7b).—A solution of sodio methylmalonic ester was prepared by stirring diethyl methylmalonate (36 mmol, 6.15 ml) with sodium hydride (36 mmol) in DMSO (75 ml) for 1 hr. 9-Nitroanthracene (18 mmol, 4.02 g) and DMSO (50 ml) were added, and after 1 hr the reaction mixture was poured over 500 ml of ice–water and acidified. Crude product was collected by filtration and dissolved in CH_2Cl_2 (75 ml). The solution was washed twice with water, dried (Na_2SO_4), decolorized, and concentrated to 30 ml. The volume of the solution was then maintained by the addition of ethanol as CH_2Cl_2 was removed at the steam bath. After several hours at −15°, 5.40 g (75%) of slightly yellow crystals had been deposited. Recrystallization from CH_2Cl_2–ethanol gave **7b** as white crystals:[23] mp 113–114°; ir 1733, 1555, 1292, 1258, 1108, 742 cm^{-1}; mass spectrum *m/e* (*I*) 223.0632 (75, $C_{14}H_9NO_2$), 193 (60), 178.0784 (100, $C_{14}H_{10}$), 129 (73), 74 (65).

Anal. Calcd for $C_{22}H_{23}NO_6$: C, 66.49; H, 5.83; N, 3.52. Found: C, 66.49; H, 5.85; N, 3.39.

9-Nitro-10-(2-nitro-2-propyl)-9,10-dihydroanthracene (7c).—A solution of sodium methylsulfinylmethide was prepared by stirring sodium hydride (36 mmol) with DMSO (50 ml) at 70° until gas evolution had subsided. 2-Nitropropane (36 mmol, 3.2 ml) was added in portions while the temperature was maintained at 70°, and stirring was continued for 30 min after addition was complete. The thick paste which resulted upon cooling was diluted with a solution of 9-nitroanthracene (18 mmol, 4.02 g) in warm DMSO (75 ml), and nearly all of the solid dissolved within the first few min. After 1 hr the reaction mixture was poured over 300 ml of ice–water, and concentrated HCl was added until a persisting green color was produced (pH *ca.* 4). The precipitate was collected by filtration and dissolved in CH_2Cl_2; the solution was washed, dried, decolorized, and concentrated.[24] Hexane was added as the last of the CH_2Cl_2 was removed at the steam bath. The pink crystals obtained upon cooling of the solution weighed 4.29 g (76%). Two more recrystallizations gave **7c** as white crystals: mp 130–140° dec (with gas evolution); ir 1550, 1530,

---

[19] R. H. Williams, Ph.D. Thesis, University of Illinois, Urbana, Ill., 1971.

[20] Exact mass measurements were obtained by the peak-matching technique by Mr. J. Carter Cook on an MAT SM-1B high resolution mass spectrometer and are within 0.0004 amu of values calculated for the indicated ion composition. We gratefully acknowledge NIH grants GM-16864 and CA-11388 to the Department of Chemistry and Chemical Engineering, University of Illinois, which helped make purchase of the SM-1B possible.

[21] Commercially available reagents were used as received. Melting points were determined with a Kofler micro stage apparatus and are uncorrected. A Perkin-Elmer 521 ir spectrophotometer was used for ir spectra, which were run in KBr. Microanalyses were performed by Mr. J. Nemeth and associates. Routine nmr spectra were recorded on a Varian A-56/60 or A-60A spectrometer; 100-MHz and 220-MHz spectra were recorded by Mr. R. L. Thrift and associates on Varian HA-100 and HR-220[9] spectrometers, respectively. Mass spectra were recorded by Mr. J. Wrona and associates on an Atlas CH4 mass spectrometer at 70 eV.

[22] Intensities are reported as per cent of base peak.

[23] Highly purified samples of crystalline **7b** decompose upon standing at room temperature for several weeks. The rate of decomposition can be retarded by storing adduct **7b** at −15°.

[24] Alternatively, washing the crude material with several portions of ethanol affords product of purity which is adequate for most purposes.

1370, 1350, 1340, 725 cm^{-1}; mass spectrum *m/e* (*I*) 208.0763 (24, $C_{14}H_{10}NO$), 91 (32), 60 (100), 58 (84), 55 (26).

Anal. Calcd for $C_{17}H_{16}N_2O_4$: C, 65.37; H, 5.16; N, 8.97. Found: C, 65.15; H, 5.01; N, 8.89.

9-Nitro-10-dicyanomethyl-9,10-dihydroanthracene (7d).—A solution of sodio malononitrile was prepared by adding a solution of malononitrile (36 mmol, 2.38 g) in DMSO (5 ml) to a magnetically stirred suspension of sodium hydride (36 mmol) in DMSO (45 ml). After gas evolution had ceased (*ca.* 1 hr), 9-nitroanthracene (18 mmol, 4.02 g) and DMSO (75 ml) were added. The reaction mixture was stirred for 2 hr prior to aqueous work-up. The crude product was dissolved in CH_2Cl_2 (75 ml), and the solution was washed, dried, decolorized, and concentrated on the steam bath until crystallization began. The light yellow product (2 crops) weighed 3.68 g (70%). Recrystallization from CH_2Cl_2–cyclohexane gave **7d** as white crystals: mp 166–170° dec (with gas evolution); ir 2910, 1555, 1490, 1360, 755, 705 cm^{-1}; mass spectrum *m/e* (*I*) 223.0632 (79, $C_{14}H_9NO_2$), 178.0784 (55, $C_{14}H_{10}$), 176 (50), 84 (58), 66 (100).

Anal. Calcd for $C_{17}H_{11}N_3O_2$: C, 70.57; H, 3.83; N, 14.53. Found: C, 70.53; H, 3.79; N, 14.70.

10-Dicarbethoxymethyl-9,10-dihydro-9-oximinoanthracene (10a).—The preparation of **7a** was repeated, but, 1 hr after the addition of 9-nitroanthracene, benzyl chloride (72 mmol, 8.3 ml) was added, and the reaction mixture was stirred at room temperature for an additional 15 hr before aqueous work-up. The yellow precipitate was collected by filtration, washed with cold ethanol (three 40-ml portions) and recrystallized from CH_2Cl_2–hexane. The light yellow product weighed 4.18 g (63%). Recrystallization from ethanol gave **10a** as white crystals: mp 196–199° dec; ir 1750, 1727, 1305, 1252, 1181, 977 cm^{-1}; mass spectrum *m/e* (*I*) 208.0758 (100, $C_{14}H_{10}NO$), 207 (95), 190 (22), 177 (21), 121 (36), 120 (56), 117 (28).

Anal. Calcd for $C_{21}H_{21}NO_5$: C, 68.65; H, 5.76; N, 3.81. Found: C, 68.61; H, 5.60; N, 3.99.

10-(1,1-Dicarbethoxyethyl)-9,10-dihydro-9-oximinoanthracene (10b).—To a magnetically stirred solution of sodio methylmalonic ester (prepared from diethyl methylmalonate (18 mmol) and sodium hydride (18 mmol)) in DMSO (25 ml) were added 9-nitroanthracene (18 mmol, 4.02 g) and DMSO (25 ml). After 1 hr, benzyl bromide (18 mmol, 2.14 ml) was added, and stirring was continued for 2 hr before aqueous work-up. The precipitate was dissolved in CH_2Cl_2, and the solution was washed, dried, decolorized, and concentrated to a volume of 30 ml. Volume of the solution was then maintained by the addition of ethanol as remaining CH_2Cl_2 was removed at the steam bath. The ethanol solution was allowed to cool slowly and maintained at −15° for 4 hr. The supernatant liquid was decanted, and the crystals were washed twice with cold ethanol (10-ml portions). The yellow crystalline product, which weighed 1.05 g, was identified as 9-nitroanthracene by melting point (147–149.5°), mixture melting point and tlc (recovery, 26%). The combined mother liquor and washings were concentrated to the original volume (30 ml) and cooled to −15°. Crystallization was initiated by scratching and after 5 hr the product was collected by filtration and washed with cold ethanol. The slightly yellow crystals weighed 3.40 g (68.5%, based on unrecovered nitroanthracene) and melted at 161–163.5°. Recrystallization from CH_2Cl_2–ethanol gave **10b** as white crystals: mp 162.5–163.5°; ir 1730, 1250, 1230, 1112, 1100, 780 cm^{-1}; mass spectrum *m/e* (*I*) 209 (11), 208.0763 (100, $C_{14}H_{10}NO$), 207 (11), 191 (14), 190 (25), 180 (13).

Anal. Calcd for $C_{22}H_{23}NO_5$: C, 69.27; H, 6.08; N, 3.67. Found: C, 69.14; H, 5.98; N, 3.62.

10-(2-Nitro-2-propyl)-9,10-dihydro-9-oximinoanthracene (10c).—A solution of 9-nitroanthracene (18 mmol, 4.02 g) in warm DMSO (75 ml) was added to a magnetically stirred suspension of sodium propanenitronate (prepared from 36 mmol each of 2-nitropropane and sodium hydride) in 100 ml of DMSO. After 30 min of reaction, benzyl chloride (36 mmol, 4.15 ml) was added, and the reaction mixture was stirred for 15 hr before aqueous work-up. The precipitate was collected by filtration and washed with three 40-ml portions of ethanol and one 40-ml portion of CH_2Cl_2. The white crystals of **10c** weighed 3.15 g (59%) and decomposed at 230–240°: ir 1535, 1395, 1350, 1000, 935, 750 cm^{-1}; mass spectrum *m/e* (*I*) 209 (16), 208.0763 (100, $C_{14}H_{10}NO$), 191 (11), 190 (18), 180 (10).

Anal. Calcd for $C_{17}H_{16}N_2O_3$: C, 68.90; H, 5.44; N, 9.45. Found: C, 69.00; H, 5.44; N, 9.23.

9-(Dicarbethoxymethyl)anthracene (12a).—Hydrochloric acid (24 mmol, 2 ml) was added to a magnetically stirred solution of **7a** (1.0 mmol, 383 mg) in 33% aqueous ethanol (60 ml) at the boiling point. The volume of the reaction mixture was maintained by the addition of water as ethanol was distilled during 1 hr. The reaction mixture was cooled to room temperature, and the precipitate was collected by filtration. The light yellow crystals weighed 311 mg (93%). Recrystallization from methylcyclohexane gave **12a** as light yellow crystals: mp 121–123°; ir 1750, 1705, 1250, 1200, 1032, 740 cm^{-1}; nmr (CS_2) δ 7.4–8.5 (m, aromatic), 5.9 [s, $CH(CO_2Et)_2$], 4.1 (q, J = 7 Hz, CH_2CH_3), 1.1 (t, J = 7 Hz, CH_2CH_3); mass spectrum *m/e* (*I*) 336 (100), 236 (91), 235 (41), 191 (57), 189 (43).

Anal. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 75.13; H, 6.15.

(9-Anthryl)acetic Acid.—Water (20 ml) was added to a refluxing solution of **12a** (1.0 mmol, 336 mg) and sodium hydroxide (5.0 mmol, 200 mg) in ethanol (30 ml). The solution was heated under reflux for 4 hr, and the volume of the solution was maintained by addition of water as ethanol was boiled off during a fifth hour of heating. Hydrochloric acid (12 mmol, 1.0 ml) was added to the aqueous solution, and the reaction mixture was heated under reflux for 1 hr to complete decarboxylation. The product was collected by filtration and recrystallized from acetic acid. The light yellow crystals weighed 193 mg (82%). Recrystallization from benzene gave (9-anthryl)acetic acid as light yellow crystals: mp 227–229° dec (lit.[18] mp 229–231.4°); ir 1700, 1305, 728 cm^{-1}.

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.43; H, 5.31.

9-(1,1-Dicarbethoxyethyl)anthracene (12b).—Hydrochloric acid (48 mmol, 4 ml) was added to a refluxing solution of **7b** (2.0 mmol, 794 mg) in ethanol (40 ml). After 1 hr, the reaction mixture was poured into 300 ml of water, and the resulting suspension was extracted with CH_2Cl_2 (three 50-ml portions). The extract was washed, dried, decolorized, and concentrated. The last of the CH_2Cl_2 was replaced with ethanol (95%) at the steam bath, and the volume of the solution was reduced to 4 ml. After 12 hr at −15°, 326 mg (46.5%) of yellow crystals had been deposited. Recrystallization from CH_2Cl_2–ethanol gave **12b** as yellow crystals: mp 155–156.5°; ir 1740, 1700, 1380, 1268, 1117, 741 cm^{-1}; nmr (CS_2) δ 7.2–8.3 (m, aromatic), 4.0 (m, CH_2CH_3), 2.1 [s, $C(CH_3)(CO_2Et)_2$], 1.0 (t, J = 7 Hz, CH_2CH_3); mass spectrum *m/e* (*I*) 350 (100), 277 (62), 203 (100), 202 (32), 138 (32).

Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.40; H, 6.22.

10-(2-Nitro-2-propyl)-9,10-dihydro-9-oxoanthracene (13).—Dilute hydrochloric acid (3.0 ml concentrated hydrochloric acid and 40 ml of water) was added to a magnetically stirred solution of **7c** (2.0 mmol, 624 mg) in refluxing ethanol (40 ml). After 2 hr at reflux, the reaction mixture was poured over 100 ml ice-water, and the resulting suspension was filtered. The filtrate was extracted with CH_2Cl_2 (four 25-ml portions), the extract was washed twice with water, and the precipitate was washed with the extract. The precipitated weighed 166 mg (28%), and was identified as oxime **10c** by tlc and ir. The filtrate was concentrated to a volume of 4 ml, and the remaining CH_2Cl_2 was replaced with ethanol at the steam bath. After the solution had stood for several hr at −15°, 180 mg (32%) of **13** was deposited. Recrystallization from CH_2Cl_2–ethanol gave **13** as white crystals: mp 185.5–187°; ir 1665, 1600, 1525, 1305, 1285, 730 cm^{-1}; nmr ($CDCl_3$) δ 7.3–8.3 (m, aromatic), 4.9 (s b, $CHCMe_2NO_2$), 1.3 [s, $C(CH_3)_2NO_2$]; mass spectrum *m/e* (*I*) 194 (18), 193.0656 (100, $C_{14}H_9O$), 165 (13).

Anal. Calcd for $C_{17}H_{15}NO_3$: C, 72.58; H, 5.38; N, 4.98. Found: C, 72.83; H, 5.39; N, 4.94.

Registry No.—**1**, 602-60-8; **7a**, 29925-28-8; **7b**, 29925-29-9; **7c**, 29925-30-2; **7d**, 29925-31-3; **10a**, 29925-32-4; **10b**, 29925-33-5; **10c**, 29925-34-6; **12a**, 29925-36-7; **12b**, 29925-36-8; **13**, 29925-37-9.