

Application of the Hammett Equation to Nonaromatic Unsaturated Systems.

XII. Reactivity and Physical Properties of the Ethynyl Proton

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Received April 21, 1972

Data for rates of hydrogen-deuterium and hydrogen-tritium exchange in substituted acetylenes, equilibrium constants for complex formation between substituted acetylenes and diethyl acetamide, CH stretching frequencies in the infrared spectra of substituted acetylenes, and chemical shifts of substituted acetylenes were correlated with the extended Hammett equation, $Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h$. Of the 16 sets correlated with the extended Hammett equation, 14 gave statistically significant results. The correlations clearly demonstrated that the resonance effect is in all cases an important and, in some, the predominant component of the electrical effect.

We have for some time been interested in the application of linear free energy relationships to structure-reactivity problems, involving nonaromatic unsaturated systems.¹⁻¹⁴ In this work we extend our investigations to substituent effects upon the reactivity and physical properties of the ethynyl proton. There have been several attempts to correlate data for rates of hydrogen-deuterium exchange^{15,16} and hydrogen-tritium exchange¹⁷ of $\text{XC}\equiv\text{CH}$ with the Taft equation. Values of k_0 for complex formation between $\text{XC}\equiv\text{CH}$ and *N,N*-diethylacetamide are said to be linear in the Taft σ^* constants.¹⁸ We have reported the application of the Hammett equation to ionization constants of substituted propiolic acids, rates of alkaline hydrolysis of substituted ethyl propiolates, and dipole moments of substituted acetylenes and acetylene derivatives using the σ_p constants. No previous attempts to apply the extended Hammett equation (eq 1) to data for compounds of the

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \quad (1)$$

type $\text{XC}\equiv\text{CH}$ are extant in the literature. To remedy this deficiency we have correlated rates of hydrogen-deuterium and hydrogen-tritium exchange, equilibrium constants for complex formation, C-H stretching frequencies, and nmr chemical shifts for ethynyl protons with eq 1. The data used are set forth in Table I. The σ_I constants required are generally

taken from our compilation.¹⁹ The σ_R constants were obtained from eq 2 using the σ_p values reported by

$$\sigma_R = \sigma_p - \sigma_I \quad (2)$$

McDaniel and Brown²⁰ whenever possible. Substituent constants were also obtained from previous papers in this series.¹⁻¹⁴ Substituent constants taken from other sources are reported in Table II. Correlations were carried out by multiple linear regression analysis.²¹

Another function of this investigation is the determination of the composition of the electrical effect of substituents upon the reactivity of the ethynyl proton. In this system, resonance interaction between substituent and reaction site is not possible. Superficially, the system might be expected to show a substituent effect composition analogous to that of the σ_p constants which were defined from the system $4\text{-X-C}_6\text{H}_4\text{CH}_2\text{Y}$ where the substituent is also incapable of resonance interaction with the reaction site, Y.

Results

The results of the correlations are presented in Table III. Of the four sets of rates of hydrogen-deuterium or hydrogen-tritium exchange one gave excellent, one gave good, and one gave fair correlation. The other set did not give a significant correlation. Of the three sets of equilibrium constants for hydrogen-bonded complex formation with dimethylacetamide, one gave very good, one gave good, and one gave fair correlation. Of the five sets of infrared C-H stretching frequencies, three gave excellent, one gave very good, and one gave good correlation. Of the four sets of nmr chemical shifts two gave good and one gave fair correlation. The other set did not give a significant correlation. Set 16 was correlated with the inclusion (set 16A) and exclusion (set 16B) of the values for the formyl, phenyl, and vinyl substituents. A slight improvement was noted for set 16B over 16A. Thus, overall, of the 16 sets correlated with eq 1, 14 gave significant results.

For purposes of comparison, a set of data consisting of partial rate factors for hydrogen-deuterium exchange at the para position of substituted benzenes

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- (3) M. Charton, *J. Org. Chem.*, **26**, 735 (1961).
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- (6) M. Charton, *ibid.*, **30**, 557 (1965).
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- (9) M. Charton, *ibid.*, **31**, 3745 (1966).
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- (12) M. Charton, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13-18, 1969, p 59-O.
- (13) M. Charton, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 12-17, 1971, p 140-P.
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(21) K. A. Brownless, "Statistical Theory and Methodology in Science and Engineering," 2nd ed, Wiley, New York, N. Y., 1965; E. L. Crow, F. A. Davis, and M. W. Maxfield, "Statistics Manual," Dover Publications, New York, N. Y., 1960.

TABLE I
 DATA USED IN CORRELATIONS

1. Rates of hydrogen-deuterium exchange for substituted acetylenes in 90% (v/v) acetone-water at 21°^a
t-BuS, 910; MeO, 63; *t*-Bu, 2.1; C₂H₃S, 4000
2. Rates of hydrogen-deuterium exchange for substituted acetylenes in 88.5% (v/v) methanol-water at 21°^a
t-BuS, 64; MeO, 15; *t*-Bu, 0.8; C₂H₃S, 430; C₂H₃O, 60
3. Rates of hydrogen-deuterium exchange for substituted acetylenes in dimethylformamide, 5 M in D₂O containing triethylamine, at 40°^b
 Ph, 6.6; H, 4.8; Bu, 0.38; MeO, 130; Ph₃Si, 450
4. Rates of hydrogen-tritium exchange for substituted acetylenes in 1:4 (v/v) methanol-water at 25°^c
 BrCH₂, 430; ClCH₂, 490; ICH₂, 265; Ph, 250; Me₃Si, 66; PhCH₂, 25; *i*-Pr, 12.3; Bu, 9.7; BuCH₂CH₂, 9.4; *t*-Bu, 8.9; *t*-BuCH₂, 7.0
5. Equilibrium constants for complex formation of substituted acetylenes with diethylacetamide in squalane at 28°^d
 BuCH₂, 0.60; *t*-Bu, 0.60; Me₃Si, 0.65; ClCH₂, 1.54; BrCH₂, 1.50
6. Equilibrium constants for complex formation of substituted acetylenes with diethylacetamide in squalane at 0°^d
t-Bu, 0.96; Me₃Si, 1.12; ClCH₂, 2.78; BrCH₂, 2.74
7. Equilibrium constants for complex formation of substituted acetylenes with diethylacetamide in squalane at 25°^d
t-Bu, 0.58; Me₃Si, 0.66; ClCH₂, 1.73; BrCH₂, 1.67; BuCH₂, 0.60
8. CH stretching frequencies for substituted acetylenes in hexane^e
 ClCH₂, 3318; 4-MeOC₆H₄, 3323; Ph, 3323; 4-O₂NC₆H₄, 3319; Bz, 3306; EtO₂C, 3310; EtO, 3339; BrCH₂, 3316; BuCH₂CH₂, 3319
9. CH stretching frequencies of substituted acetylenes in diethyl ether^e
 ClCH₂, 3317; Ph, 3320; Bz, 3304; EtO₂C, 3309; BrCH₂, 3315; BuCH₂CH₂, 3317
10. CH associated stretching frequencies of substituted acetylenes in diethyl ether^e
 ClCH₂, 3250; Ph, 3250; Bz, 3219; EtO₂C, 3320; BrCH₂, 3250; BuCH₂CH₂, 3267
11. CH stretching frequency differences of substituted acetylenes in dimethylacetamide^f
 Bu, 74; Ph, 91; ClCH₂, 94; MeO, 81; EtO₂C, 123; BrCH₂, 94; BuCH₂, 74; BuCH₂CH₂, 72
12. CH stretching frequencies of substituted acetylenes in dimethylacetamide^f
 Bu, 3314; Ph, 3314; ClCH₂, 3314; MeO, 3328; EtO₂C, 3306; BrCH₂, 3313; BuCH₂, 3314; BuCH₂CH₂, 3314; CN, 3304
13. Proton chemical shifts of substituted acetylenes^g
 Me, -1.76; Pr, -1.79; Bu, -1.73; CHO, -1.89; CH₂OH, -2.33; CH₂I, -2.19; CH₂Br, -2.33; CH₂Cl, -2.40; C₂H₃, -2.92; Ph, -2.93; EtS, -2.64; EtO, -1.33
14. Proton chemical shifts of substituted acetylenes (vapor phase)^g
 H, 1.50; Me, 1.56; Et, 1.59; HC₂, 1.48; Pr, 1.72; *t*-Bu, 1.75; CHO, 2.75; Ac, 3.00
15. Proton chemical shifts of substituted acetylenes in CCl₄^h
 Me, 1.76; Et, 1.78; HC₂, 2.01; Pr, 1.75; *t*-Bu, 1.87; CHO, 3.28; Ac, 3.03
16. Proton chemical shifts of substituted acetylenes in CCl₄^h
 H, 8.20; Pr, 8.21; Bu, 8.27; BuCH₂, 8.25; ClCH₂, 7.60; BrCH₂, 7.67; ICH₂, 7.81; HOCH₂, 7.67; MeOCH₂, 7.63; PhOCH₂, 7.99; CHO, 8.11; Ph, 7.07; C₂H₃, 7.08; HO-CH₂CH₂, 8.08
21. Partial rate factors for hydrogen-deuterium exchange with KNH₂ in NH₃ (1)ⁱ
 F, 100; CF₃, 10,000; PhO, 4; Ph, 2.9; Me₂N, 0.07; H, 1; Me, 0.4; MeO, 0.5

^a W. Drenth and A. Loewenstein, *Recl. Trav. Chim. Pays-Bas*, **81**, 635 (1962). ^b R. E. Dessy, Y. Okuzumi, and A. Chen, *J. Amer. Chem. Soc.*, **84**, 2899 (1962); ^c C. Eaborn, G. A. Skinner, and D. R. M. Walton, *J. Chem. Soc. B*, 989 (1966). ^d R. Queignec and B. Wojtkowiak, *Bull. Soc. Chim. Fr.*, 860 (1970). ^e J. C. Brand, G. Eglinton, and J. F. Morman, *J. Chem.*

Soc., 2526 (1960). ^f R. West and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, **83**, 765 (1961). ^g P. Jouve, Thesis, Faculte des Science de l'Université de Paris, Paris, 1966, p 23. ^h M. M. Kreevoy, H. B. Charman, and D. R. Vinard, *J. Amer. Chem. Soc.*, **83**, 1978 (1961). ⁱ A. I. Shatenshtein, *Tetrahedron*, **18**, 95 (1962).

(set 21) was correlated with eq 1. Excellent results were obtained for this correlation.

Discussion

Substituent Effects on the Acidity of the Ethynyl Proton.—The two factors which characterize the nature of a substituent effect are its composition and its magnitude. The composition of the electrical effect may be described in terms of the quantity P_R , where²²

$$P_R = \frac{100\beta}{\alpha + \beta} \quad (3)$$

Table IV lists P_R values for the sets studied here.

The values of P_R obtained for the hydrogen-deuterium exchange (sets 1 and 2) show clearly the presence of a significant resonance effect. This conclusion is supported by the results obtained for the hydrogen-tritium exchange, for which a very much greater value of P_R is obtained. We have previously noted that the composition of the substituent effect upon the ethynyl proton might be expected to be compar-

(22) M. Charton, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13-18, 1969, p 17-P.

 TABLE II
 SUBSTITUENT CONSTANTS

X	σ_I	Ref	σ_R	Ref
<i>t</i> -BuS	0.23	<i>a</i>	-0.21	<i>b</i>
C ₂ H ₃ S	0.27	<i>a</i>	-0.15	<i>b</i>
C ₂ H ₃ O	0.35	<i>a</i>	-0.50	<i>b</i>
Ph ₃ Si	-0.07	<i>c</i>	0.17	<i>c</i>
<i>t</i> -BuCH ₂	-0.02	<i>a</i>	-0.15	<i>a</i>
BuCH ₂ CH ₂	-0.04	<i>a</i>	-0.11	<i>a</i>
4-MeOC ₆ H ₄	0.09	<i>d</i>	-0.18	<i>e</i>
4-O ₂ NC ₆ H ₄	0.22	<i>d</i>	0.01	<i>e</i>
HC ₂	0.35	<i>f</i>	-0.09	<i>f</i>
CH ₂ CH ₂ OH	0.00	<i>g</i>	-0.10	<i>a</i>
PhOCH ₂	0.13	<i>a</i>	-0.06	<i>a</i>

^a Estimated as described in M. Charton, Abstracts, 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug 30-Sept 4, 1964, p 56-V. ^b Calculated from the σ_p value estimated by the method of M. Charton, *J. Org. Chem.*, **28**, 3121 (1963). ^c Calculated from σ_m and σ_p values reported by R. A. Benkeser, C. E. DeBoer, R. E. Robinson, and D. M. Sauve, *J. Amer. Chem. Soc.*, **78**, 682 (1956). ^d Calculated from the pK_a for 4-XC₆H₄CH₂CO₂H. ^e Calculated from σ_p values reported by E. Berlner and L. H. Liu, *J. Amer. Chem. Soc.*, **75**, 2417 (1953). ^f M. Charton in "The Chemistry of the Alkenes," Vol. 2, J. Zabicky, Ed., Wiley-Interscience, London, 1970, p 511. ^g Calculated from the pK_a of HOCH₂CH₂CH₂CO₂H.

TABLE III

Set	RESULTS OF CORRELATIONS										
	α	β	h	R^a	F^b	r^c	s_{est}^d	s^d	s^d	s_h^d	n^e
1	6.86	4.41	2.37	0.9991	286.8 ^k	0.434	0.0755	0.0301 ^k	0.267 ^k	0.0747 ^k	4
2	7.74	3.46	0.909	0.990	51.88 ⁱ	0.595	0.197	0.762 ^h	0.637 ^k	0.183 ^k	5
3	12.3	7.26	1.22	0.694	0.930 ^m	0.910 ^f	1.13	10.5 ^o	5.36 ^o	0.569 ⁿ	5
4	5.59	6.55	2.08	0.969	62.75 ^f	0.011	0.204	0.613 ^f	1.05 ^f	0.113 ^f	11
5	1.53	0.828	-0.0362	0.993	72.94 ⁱ	0.114	0.0354	0.129 ^h	0.237 ^l	0.0203 ^o	5
6	1.63	0.891	0.211	0.999	217.9 ^k	0.240	0.0205	0.0783 ^k	0.155 ⁿ	0.0119 ^k	4
7	1.73	0.995	-0.0130	0.995	100.0 ^h	0.114	0.0343	0.125 ^h	0.230 ^k	0.0197 ^p	5
8	-0.791	-47.8	3315	0.989	89.08 ^f	0.156	1.92	6.11 ^q	3.63 ^f	1.41 ^f	7
9	11.8	-60.8	33.11	0.970	23.91 ⁱ	0.870 ^e	1.88	12.5 ^o	14.5 ^k	2.32 ^f	6
10	-74.3	-78.6	3255	0.981	37.77 ^h	0.870 ⁱ	4.82	32.1 ⁿ	37.1 ⁿ	5.96 ^f	6
11	-4.27	-34.7	3311	0.981	77.05 ^f	0.283	1.49	2.67 ⁿ	3.06 ^f	0.776 ^f	9
12	97.1	50.4	82.9	0.991	135.0 ^f	0.009	2.70	7.05 ^f	5.69 ^f	1.42 ^f	8
13	-0.355	-1.31	-2.30	0.367	0.702 ^m	0.127	0.514	1.21 ^p	1.11 ^o	0.240 ^f	12
14	0.328	4.08	2.02	0.883	8.874 ⁱ	0.635	0.334	0.836 ^p	1.37 ^k	0.166 ^h	8
15	1.02	3.48	2.22	0.929	12.56 ⁱ	0.676	0.297	0.798 ^o	1.28 ^f	0.171 ^f	7
16A	-3.79	5.30	8.47	0.712	5.669 ^k	0.702 ^h	0.307	1.19 ^h	1.77 ⁱ	0.207 ^f	14
16B	-2.51	-0.137	8.08	0.797	6.942 ^k	0.477	0.184	0.776 ⁱ	1.85 ^q	0.169 ^f	11
21	6.20	3.01	0.270	0.951	23.59 ^o	0.140	0.599	1.09 ^h	0.655 ^h	0.361 ^o	8

^a Multiple correlation coefficient. ^b F test for significance of regression. ^c Partial correlation coefficient of σ_I on σ_R . ^d Standard errors of the estimate, α , β , and h . ^e Number of points in set. ^f 99.9% confidence level (CL). ^g 99.5% CL. ^h 99.0% CL. ⁱ 98.0% CL. ^j 97.5% CL. ^k 95.0% CL. ^l 90.0% CL. ^m 90% CL. ⁿ 80.0% CL. ^o 50.0% CL. ^p 20% CL. ^q 20% CL.

TABLE IV
VALUES OF P_R

Set	P_R	Set	P_R	Set	P_R
1	39	7	36	12	34
2	31	8	b	13	a
3	a	9	b	14	b
4	54	10	c	15	b
5	35	11	b	16	d
6	d			21	33

^a Correlation was not significant for this set. ^b α was not significant for this set. ^c α and β were not significant for this set. ^d β was not significant for this set.

able to that of the σ_p constants, for which P_R is 40. This does indeed seem to be the case. It is of interest to compare the values of P_R obtained for rates of hydrogen-deuterium exchange on substituted acetylenes with rates of hydrogen-deuterium exchange on other systems. Of particular interest is exchange at the ortho and para positions of substituted benzenes. Data are available for the rates of hydrogen-deuterium exchange of substituted benzenes in liquid ammonia. The solvent is not the same as that used for the substituted acetylenes and this may very well affect the P_R value for exchange at the ortho position. The composition of the electrical effect for exchange at the para position should be independent of solvent, however. That this is the case may readily be seen from the following argument. Data for a wide variety of para-substituted benzene set types have been correlated in various solvents by the σ_p constants. For a substituent constant σ_X , we may write

$$P_R = \frac{100\delta}{\lambda + \delta} \quad (4)$$

where

$$\sigma_X = \lambda\sigma_{I,X} + \delta\sigma_{R,Y} \quad (5)$$

For σ_p , the value of P_R observed is 50. Since data in various solvents are all correlated by the σ_p constants with P_R of 50, obviously the composition of the electrical effect is independent of solvent. This does not mean that α and β for para-substituted benzenes are

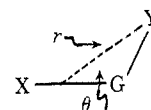
independent of solvent, but simply that they vary in such a way that their ratio, and therefore P_R , is a constant.

The value of P_R obtained for the ortho position is 5.7.²³ Clearly, the localized effect is by far the predominant factor. This is in sharp contrast to the behavior of the substituted acetylenes. It is presumably due to the different geometries of the two systems. In the exchange at the ortho position, the reaction site is almost in contact with the substituent, whereas in the substituted acetylenes, two carbon atoms intervene between the reaction site and the substituent. The value of P_R obtained for the rates of hydrogen-deuterium exchange in the para position of substituted benzenes is 33, in excellent agreement with the values obtained for the substituted acetylenes. This value was calculated from a correlation of partial rate factors for hydrogen-deuterium exchange of substituted benzenes with eq 1 (set 21, Tables I and III).

The magnitude of the electrical effect is measured by the magnitude of α . The value of α may be calculated from the field effect by the equation

$$\alpha_G = \frac{\cos \theta_G r^2 G^{\circ} \alpha_{G^{\circ}}}{\cos \theta_G r^2 G} \quad (6)$$

where θ and r are defined below. G refers to the skeletal group to which the substituent X and reaction site Y are bonded and G° refers to the reference skeletal group (the phenylene group).



The value of α calculated from $\alpha_{G^{\circ}}$ for set 21 is 14.2 (in liquid ammonia). The values obtained for 90% (v/v) acetone-water at 21° (set 1) and 88.5% (v/v) methanol-water at 21° (set 2) are 6.86 and 7.74, respectively. The difference in α values can be ascribed to the differences in medium and in temperature. The value of α obtained for hydrogen-tritium exchange in

methanol-water at 25° (set 4) is 5.59, in fairly good agreement with the value of α for hydrogen-deuterium exchange in methanol-water at 21° of 7.74.

Another measure of the acidity of the ethynyl proton is provided by the data for complex formation of substituted acetylenes with diethylacetamide. The values of P_R obtained for these data (sets 5 and 7) are 35 and 36, respectively, in excellent agreement with the values of P_R obtained for hydrogen-deuterium exchange of substituted acetylenes. The magnitude of the localized effect in these sets is much smaller than that observed for hydrogen-deuterium or hydrogen-tritium exchange; the values are 1.53, 1.63, and 1.73. Obviously the complex formation is much less sensitive to substituent effects. The same effect is observed in a comparison of the magnitude of α for complex formation of 2-substituted pyridines with phenols with α for ionization of 2-substituted pyridinium ions (1.43 and 11.4, respectively).

Infrared C-H Stretching Frequencies.—The resonance effect is predominant in the majority of the sets of infrared C-H stretching frequencies, although the C-H stretching frequencies of substituted acetylenes in dimethylacetamide (set 12) show a P_R value of 34, in good agreement with those observed for hydrogen-deuterium exchange and for complex formation with diethylacetamide. There is no explanation known to us for the predominance of the resonance effect in sets 8, 9, and 11. Comparable studies of C-H stretching frequencies as a function of substituent variation do not seem to be extant for substituted benzenes or ethylenes. It should be noted that C-H stretching frequencies involve very small changes. In any case,

the importance of the resonance effect in these data is obvious.

Nmr Proton Chemical Shifts.—We have previously observed that proton chemical shifts of cis and trans protons in substituted ethylenes are successfully correlated by eq 1. It therefore seemed of interest to study the proton chemical shifts of substituted acetylenes. Although significant correlations were obtained for three of the four sets studied (sets 14, 15, and 16B), the results are not particularly good. Excluding set 16B, in which the substituents are all of the type $-\text{CH}_2\text{X}$, and therefore there is no dependence on the resonance effect, the results are in good agreement with the majority of the sets of infrared frequencies studied and in accord with the values of P_R observed for proton chemical shifts of cis and trans protons in substituted ethylenes.¹³ As regards the magnitude of the resonance effect, it is larger for proton chemical shifts in substituted acetylenes (β 4.08 and 3.48 for sets 14 and 15, respectively) than it is for either trans protons (β 2.11) or cis protons (β 2.20) in substituted ethylenes.¹³ As the correlation of proton chemical shifts for substituted acetylenes failed with the most extensive set of substituents studied (set 13), the conclusion we have arrived at can only be regarded as qualitative.

Conclusion

Overall, the results obtained clearly show that resonance effects are important in determining the reactivity and physical properties of the ethynyl proton. They also demonstrate the applicability of eq 1 to data for substituted acetylenes.

A Synthesis of 2,3-Dihydro-1H-cyclopenta[a]chrysene¹

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Received June 14, 1971

2,3-Dihydro-1H-cyclopenta[a]chrysene (**13**) has been synthesized from 9,10-dihydrophenanthrene by a ten-step reaction sequence. The peripheral benzo ring atoms arise from succinic acid by a Haworth-type reaction sequence and the cyclopenteno atoms from carboethoxyethanoyl chloride by a Friedel-Crafts condensation, leading after several steps (7-9) to the key intermediate, 2-(3-carboxypropyl)-7-(2-carboxyethyl)phenanthrene (**10**), which was cyclized to give a mixture of products. The major constituent, established as the pentacyclic diketone, 2,3,8,9,10,11-hexahydro-1H-cyclopenta[a]chrysene-1,11-dione (**11**) by spectroscopic evidence, was converted to the final product (**13**) by reduction and dehydrogenation. Several examples of Friedel-Crafts acylation with carboethoxyethanoyl chloride are described.

In 1943 Ruzicka and coworkers² dehydrogenated quinovic acid and isolated among other products two aromatic hydrocarbons which were assumed to be alkylcyclopentenchrysenes. Since quinovic acid is now known to be an ursane rather than a lupane type triterpene,³ these aromatic hydrocarbons probably have a picene rather than a cyclopentenchrysene ring

system. Nevertheless it seems possible that aromatic hydrocarbons with a cyclopentenchrysene ring system could be formed, at least in small amounts, during dehydrogenation of authentic lupane type triterpenes, just as cyclopentenchrysenes derivatives are formed by dehydrogenation of steroids. However, as yet there are no authentic reports of isolation of such substances.

Similarly, several picene type hydrocarbons, apparently formed from triterpenes during the carbonization process, have been isolated by Šorm and coworkers⁴

(1) (a) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 11-15, 1967. (b) Taken in part from the Ph.D. Dissertation of A. Silveira, Jr., University of Massachusetts, Amherst, Mass., 1962.

(2) L. Ruzicka, A. Grov, and G. Anner, *Helv. Chim. Acta*, **26**, 254 (1943).

(3) For a listing of the various types of triterpenes see T. G. Halsall and R. T. Aplin, *Fortschr. Chem. Org. Naturstoffe*, **22**, 153 (1964).

(4) V. Jarolim, K. Hejno, F. Hemmert, and F. Šorm, *Collect. Czech. Chem. Commun.*, **30**, 873 (1965).