Substituent Effects on the Ionization Equilibria of 9-Aryl-9-fluorenols and 10-Aryl-10-hydroxyanthracen-9-ones

>>

TREVOR W. TOONE, EDWARD LEE-RUFF, AND ALAN C. HOPKINSON

Department of Chemistry, York University, Downsview, Ontario M3J 1P3 Received October 10, 1974

TREVOR W. TOONE, EDWARD LEE-RUFF, and ALAN C. HOPKINSON. Can. J. Chem. 53, 1635 (1975).

The title compounds were prepared and their basicities measured. In both systems the major part of the molecule is held planar, while an aryl group is free to rotate. This may interact with the positive charge but steric hindrance to the *ortho* hydrogens may be expected to oppose planarity. In these systems no evidence was found for a reduction of the normal σ^+ value due to failure to achieve planarity. A formula is presented which gives the approximate degree of resemblance (α) of the transition state to the products and, in the case of the ionization of triarylmethanols, α is found to be linear with pK_{R^+} . It is suggested that this could resolve the apparent contradiction between the Hammett equation and the Hammond postulate.

TREVOR W. TOONE, EDWARD LEE-RUFF et ALAN C. HOPKINSON. Can. J. Chem. 53, 1635 (1975).

On a préparé les composés mentionnés dans le titre et on a mesuré leur basicité. Dans chacun des systèmes, la plus grande partie de la molécule est maintenue à l'état planaire alors que le groupe aryle est en rotation libre. Celui-ci peut interagir avec la charge positive mais on s'attend à ce que l'empêchement stérique des hydrogènes ortho s'oppose à la planarité. Dans ces systèmes, on n'a trouvé aucune preuve amenant une réduction de la valeur normale du σ^+ qui viendrait d'un empêchement à la planarité. On présente une formule qui donne un degré approximatif de ressemblance (α) de l'état de transition avec les produits et l'on trouve dans le cas de l'ionisation des triarylméthanols qu' α varie d'une façon linéaire avec le p K_R +. On suggère que ceci pourrait résoudre la contradiction apparente entre l'équation de Hammett et le postulat de Hammond. [Traduit par le journal]

The current controversy concerning the detection of unusual substrate ratios in some electrophilic aromatic substitution reactions (see ref. for summaries of opposing arguments), claimed to be the result of very early transition states, may reopen an earlier controversy which surrounded the establishment of a discrete set of Hammett-type substituent constants for use in electrophilic aromatic substitution and similar reactions. Brown and Okamoto (2) established such a set of parameters in the face of opposition (3) which claimed that such a set would be valueless because of a variable resonance effect. Deno (4) justified their use in aryl carbonium ion aryl alcohol equilibria claiming that it is not so important how much charge is delocalized in the substituent but that the amount should remain constant throughout the reaction series. Yukawa and Tsuno (5) have attempted to correlate rates and equilibria with a linear mixture of σ and σ^+ , to allow for different degrees of development of positive charge in the transition state from one reaction series to another but their method has been criticized (6) for failing to show any cor-

Can. J. Chem. Downloaded from www.nrcresearchpress.com by ARIZONA STATE UNIVERSITY on 11/10/14 For personal use only.

relation between ρ (reaction constant) and R (the fitting parameter); also, improved 'fit' may arise simply from inclusion of an extra parameter and may have no physical significance.

On the other hand, Hammond's postulate (7) requires that the more reactive the substrate, the more the transition state should be expected to resemble the reactants. In reactions in which a partial positive charge is generated in the transition state, such as the S_N1 solvolyses used to establish σ^+ (2), the reactivity is varied by changing the substituent on the phenyl group, and this in turn must change (perhaps only slightly) the position of the transition state along the reaction coordinate and the degree of positive charge generated in the transition state. Since Stock and Brown (8) have shown that σ^+ parameters do in fact correlate a large body of data, then it is likely that the movement of the transition state along the reaction coordinate is proportional from one series to another as the substituent varies. This proportionality must be included in the reaction constant, ρ , together with the usual terms measuring the suscepti-

				Analysis (%)			
Compound		Meltin	g point (°C)	Calcu	lated	Found	
No.	Aryl group	This work	Literature (ref.)	C	н	С	н
		(a) 9-A	Iryl-9-fluorenols				
1	4-Methoxyphenyl	85-86	87-88(20)	-			_
2	4-Methylphenyl	84-86	85.5-86.5(14)	_		_	
3	Phenyl	84-85	85(21)				
4	3-Methoxyphenyl	87.5-89	89-90(14)				
5	3-Chlorophenyl	79–80	81-82(14)		_	-	-
6	3-Trifluoromethylphenyl	94.5-95.5	_	73.6	4.02	73.7	4.01
		(b) 10-Aryl-10-	hydroxy-anthracen-9-or	ies	·		
7	4-Methoxyphenyl	209-210	206-207(22)	79.7	5.11	79.7	5.08
8	4-Methylphenyl	220-222	_ ` `	84.0	5.37	83.6	5.47
9	Phenyl	216-217	214(23)	-	_	-	_
10	3-Phenylphenyl	213-214	<u> </u>	86.2	5.02	86.0	5.12
11	3-Trifluoromethylphenyl	208-210	_	70.2	3.84	70.0	3.73

TABLE 1. Physical data for indicators

bility of the system to electronic influences. The effect of the former will be to make ρ less negative for these reactions, since less charge is generated in the transition state in those reactions going via a more stable carbonium ion, and the $\sigma_{effective}$ for reactive compounds will lie closer to σ than σ^+ , whereas for less reactive compounds $\sigma_{effective}$ will lie closer to σ^+ than to σ .

Unfortunately, studies of resonance effects in systems such as carbonium ions are frequently complicated by the twisting out-of-plane of aryl groups, as noted by Brown (8). A further complication could arise in cases such as the triaryl carbonium ion, in which it has been suggested (9) that two rings are twisted more than the third. Recently, however, this proposition has been contested (10). In the present study we examine the reduction of resonance through twisting of the aryl group in situations in which only one aryl group was free to rotate. We then compare our pK_{R^+} values with the previously reported rate constants for the solvolysis of 9-phenylfluorenyl chlorides.

Experimental

Indicators

Can. J. Chem. Downloaded from www.nrcresearchpress.com by ARIZONA STATE UNIVERSITY on 11/10/14 For personal use only.

9-Aryl-9-fluorenols were prepared by the addition of an ethereal solution of 9-fluorenone to the required aryl magnesium bromide. The complex so formed was broken down by treatment with dilute acid and the crude product extracted with ether, followed by crystallization from a suitable solvent.

10-Aryl-10-hydroxyanthracen-9-ones were prepared by the dropwise addition of the required aryl magnesium bromide to a rapidly stirred suspension of anthraquinone in ether under reflux. Work-up was as for the fluorenol derivatives.

Physical data on the indicators are summarized in Table 1.

Measurements

Optical densities were measured at λ_{max} of the carbonium ion in 1 cm cells on a Unicam SP1800 spectrophotometer. Stock indicator solutions were made up in Analar methanol. Aliquots of these were transferred in a 5 µl syringe to 10 ml volumetric flasks and diluted with sulfuric acid solutions of the required strength. By weighing the flask before and after each addition it was possible to correct for small differences in indicator concentration and the changes in acid strength, by using the method of Katritzky and co-workers (11).

In the case of 10-(*m*-trifluoromethylphenyl)-10-hydroxyanthracen-9-one decomposition of the indicator occurred too rapidly for the above method to be used. Instead, solutions were made up by volume, by adding 0.05 ml of stock indicator solution to exactly 10 ml of acid solution. The resulting solution was shaken rapidly and quickly transferred to a cell, a time of about 15 s. The decrease in optical density with time was followed for a further 60-100 s and the plot extrapolated back to the time of mixing. The value so obtained was uncorrected for small differences in indicator concentration but an average correction of 0.2% was applied to the acid strength.

In all cases an acid solution of approximately the same strength as the test solution was used as reference in the spectrophotometer and care was taken to keep the temperature at 25° (\pm 1), since the variation of pK_R+'s of carbinols with temperature is considerable (12).

Results and Discussion

Basicity measurements on the two series of compounds are summarized in Table 2. Both series of indicators give good linear plots of

TOONE ET AL.: HAMMETT RELATIONS

22

		Slope of log ([R ⁺]/[ROH	[])		
Compound "	$pK_{R} + b$	vsH_{R}	λ _{max} ^c	logε⁴	
1 ^e	-7.64	1.00	548	4.51	
2	-9.43	0.96	518	4.48	
3 ^{e, f}	-10.82	1.00	497	4.60	
4	-11.11	0.99	497	4.36	
5 °	-12.60	1.01	508	4.45	
6 e	-13.16	1.01	510 ^h	4.39	
7"	_	_		_	
8	-9.89	0.85	550	4.07'	
9	-10.81	0.87	530	4.21 ^{<i>i</i>}	
10	-11.15	0.87	486	4.10 ¹	
11 ^e	-12.17	0.88	534	3.95	

^aNumbering as in Table 1. ^bCalculated from $pK_R + = mH_R + \log ([R^+]/[ROH])$, following ref. 24. ^c9-Aryl-9-fluorenyl cations exhibit a visible spectrum consisting of two peaks, a smaller peak centered around 470 nm and a larger peak usually close to 520 nm. The visible spectrum of the 9-aryl-9-anthraquinonyl cation consists of two peaks, a smaller usually close to 480 nm and a larger close to 530 nm. ^dIn 96% sulfuric acid unless otherwise stated. ^eThe spectrum of the carbonium ion shows a small increase in intensity with increasing acid concentration. The method of Katritzky (ref. 25) was used to calculate ionization ratios. ^dIn acetic acid – water – sulfuric acid $pK_R + = -10.27$ and log $\varepsilon = 4.57$ (ref. 26). ^eDecomposes too quickly for measurement in sulfuric acid. ^dIn the spectrum of the carbonium ion, the shorter wavelength peak at $\lambda =$ ^dIn 18% sulfuric acid, as decomposition occurs rapidly in more concentrated acid.

acid. In 84% sulfuric acid, for reasons as in 4.

 pK_{R^+} vs. σ^+ , as shown in Fig. 1. Neither shows curvature attributable to reduced resonance through twisting of the aryl group. Since it is likely that steric hindrance to planarity of the aryl group is greatest in the 10-aryl-10-hydroxyanthracen-9-ones, it is unfortunate that 10-(pmethoxyphenyl)-10-hydroxyanthracen-9-one decomposes too rapidly in sulfuric acid for measurements to be taken, as this compound is the most likely to exhibit this effect. The reaction constants for the two series are -4.28 for the fluorenols and -2.71 for the 10-hydroxyanthra-



FIG. 1. Plot of pK_{R} + value against σ^+ constants.

cen-9-ones. The lower value in the latter case is consistent with a higher degree of solvation of these cations, which may be deduced (13) from their lower slopes of log ([R⁺]/[ROH]) vs. $-H_{R}$. It is likely that the reduced ability of substituents to delocalize the positive charge is compensated by increased interaction with the solvent.

If pK_{R^+} values of 9-aryl-9-fluorenols are compared with those of similarly substituted aryldiphenyl carbinols (14) it may be seen that joining the phenyl rings in the ortho positions reduces the stability of the associated carbonium ion by a factor of 10^4 . (The differences are 4.24 pK units for aryl = p-methoxyphenyl, 4.19 for p-methylphenyl, and 4.19 for phenyl.) This may be attributed to the introduction of 'antiaromaticity', since the joined system is effectively a dibenzocyclopentadienyl cation, a 12 π -electron system.

The solvolyses of 9-aryl-9-fluorenyl chlorides have been studied in 90% aqueous acetone at 25° (14) and the rates correlate well with σ^+ (correlation coefficient 0.995) with a reaction constant of -2.85. Similar correlation was found by Bolton et al. (15) for the solvolyses in 90:10 ethanol-acetone. Since both pK_{R^+} values and

Can. J. Chem. Downloaded from www.nrcresearchpress.com by ARIZONA STATE UNIVERSITY on 11/10/14 For personal use only.

CAN. J. CHEM. VOL. 53, 1975

Substrate	$\frac{\text{Solvent}}{\text{Solvent}} \qquad $		Correlation coefficient
9-Arÿl-9-fluorenyl chlorides ^b	90:10 ethanol-acetone ^c 90:10 acetone-water ^d 90:10 acetone-water + lithium chloride ^d	0.76 0.67 0.58	0.994 0.997 0.996
Triarylmethyl chlorides ^e	60:40 acetone-ethanol ^f	0.72	
Diarylmethyl chlorides [®]	80:20 acetone-water ^h Ethanol ^h Ethanol ⁱ Methanol ^j 2-Propanol ^j	0.71 0.81 0.77 0.83 0.73	

TABLE 3. Comparison of rates of solvolysis with basic

^e pK_R + values are for carbonium ion-alcohol equilibria. ^b pK_R + values from present work. ^cRate data from ref. 15. ^eRate data from ref. 14. ^e pK_R + values from ref. 27. ^rRate data from ref. 28. ^e pK_R + values from ref. 9. ^kRate data from ref. 30. ^rRate data from ref. 31.

logarithms of rate constants are linear with respect to σ^+ , it follows that they will be linear with respect to each other. Values of the slopes of plots of log k (from the ionization of chlorides) vs. pK_{R^+} (from the equilibrium with the carbinol) for three different series of compounds in a variety of solvents are given in Table 3.

It is reasonable to expect pK_{R^+} values of closely related compounds to vary by a constant factor in going from solvent to solvent (16); therefore the slopes of $\log k$ (solvolysis in solvent s) vs. pK_{R+} (in sulfuric acid) are probably very close to log k (in s) vs. pK_{R+} (in s). The question then arises of the reason for the less than unit slope.

Pearson and Dillon (17) examined the correlation between rates and equilibria of carbon acid ionizations and found only a rough correlation between log k (ionization) and pK_a , with a slope of approximately 0.6; this was interpreted as the degree of proton transfer from acid to base in the transition state. It is pointed out, however, that on theoretical grounds even this rough correlation is unexpected, since, in accord with Hammond's postulate (7), the weaker acids would be expected to have a greater degree of proton transfer in the transition state than the stronger acids. These data have been reexamined by Jones (18) who incorporates recent, more accurate data and shows that the plot does show the expected curvature.

Taft and co-workers (19) have measured the

rates of reaction of several triaryl carbonium ions with water and show that plots of $\log k$ (reaction) vs. pK_{R^+} were linear but only for ions containing similar substituents.

It is likely, therefore, that the slopes of about 0.7 obtained for log k (solvolysis) vs. pK_{R+} correspond to the degree to which the transition state resembles the carbonium ion, i.e. in the transition state a charge of about +0.7 is developed. It should be remembered, however, that the charge in the transition state probably varies with reactivity of the substrate, although this change is probably small over the range of reactivities in this investigation.

In an attempt to put Hammond's postulate on a more quantitative basis, the normal energy profile for a simple reaction may be greatly simplified to that of Fig. 2. Since $\tan \theta =$ $\Delta G^{\dagger}/\alpha = (\Delta G^{\dagger} - \Delta G^{0})/(1 - \alpha)$, then α , which may vary between 0 and 1 and is a rough estimate of the distance the transition state lies between reactant and product along the reaction coordinate, may be calculated using eq. 1 for those reactions for which both $\Delta G^{\overline{+}}$ and ΔG^{0}

$$\alpha = \Delta G^{*} / (2\Delta G^{*} - \Delta G^{0})$$

[1]

have been measured. One such reaction is the reaction of triaryl carbonium ions with water, for which data are collected in Table 4.

With the exception of the sesquixanthyl cation, which has an unusually low activation energy, the plot of α vs. pK_{R+} shows excellent

1638

 \mathbb{R}^{2}

Can. J. Chem. Downloaded from www.nrcresearchpress.com by ARIZONA STATE UNIVERSITY on 11/10/14 For personal use only.

TOONE ET AL .: HAMMETT RELATIONS



FIG. 2. Reaction profile in which the slope of the lines connecting the transition state with the reactants and with the products have the *same* magnitude but opposite sign.

TABLE 4. α for reaction of triaryl carbonium ions with water at 25°

Carbonium ion	pK_{R} + (ref.)	ΔG^{+} (ref.)	α
Sesquixanthyl	9.05(32)	17.6(33)	0.770
$(4-\dot{N}Me_2\cdot C_6H_4)_2C_6H_5\cdot C^+$	6.90(34)	22.5(19)	0.632
$(2,6-\text{DiMeO}\cdot\text{C}_6\text{H}_3)_3\text{C}^+$	5.88(33)	20.0(33)	0.625
$(4-NMe_2 \cdot C_6H_4)(C_6H_5)_2C^+$	4.75(34)	20.6(19)	0.593
$(2,4-\text{DiMeO}\cdot\text{C}_6\text{H}_3)_3\text{C}^+$	3.2	15.8(33)	0.580
9-(4-MeO·C ₆ H ₄)xanthyl	1.48(33)	16.3(33)	0.533
9-Phenylxanthyl	1.02(33)	15.9(33)	0.523
$(4-\text{MeO}\cdot\text{C}_6\text{H}_4)_3\text{C}^+$	0.82(27)	16.2(19)	0.518
(4-MeO·C ₆ H ₄) ₂ C ₆ H ₅ ·C ⁺	-1.02(12)	14.9(19)	0.478
$(4-\text{MeO}\cdot\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)_2\text{C}^+$	-3.51(12)	13.5(33)	0.425

"Unpublished work by K. Sano and R. W. Taft, quoted from ref. 33.

linearity, with a correlation coefficient of 0.995 and slope of 0.020 (Fig. 3). ΔG^{\pm} does not show good linearity with ΔG^{0} (correlation coefficient 0.971 excluding the sesquixanthyl cation). This is perhaps surprising in view of the success of the Hammett equation, which is frequently used to correlate free energies and activation energies of very different reactions.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by ARIZONA STATE UNIVERSITY on 11/10/14 For personal use only.

Another reaction for which data on both ΔG^{\dagger} and ΔG^{0} are available is the rate of ionization of carbon acids, for which data are collected in Table 5.

In this case the treatment is a little less successful. A plot of $\alpha vs. pK_a$ has correlation coefficient 0.962. If the data on ethyl cyanoacetate, the pK_a of which is known only approximately, and 1-chloronitroethane, the pK_a of which was determined by a different method, are omitted, the correlation coefficient for the remaining three points is 1.000.

To extend the principle to incorporate our



FIG. 3. Plot of the distance along the reaction coordinate, α , against p K_{R} + for the triarylcarbonium ions.

1640

CAN. J. CHEM. VOL. 53, 1975

TABLE 5. α for ionization of carbon acids

Carbon acid	pK _a ^a	ΔG ^{+b}	α
Nitroacetone	5.10	17.24	0.626
1-Chloronitroethane	6.80°	19.85	0.653
Ethyl nitroacetate	5.82	15.61	0.671
Ethyl cyanoacetate	~8.0	17.81	0.721
Malonitrile	11.19	15.86	0.964
^a From ref. 17 unless othe ^b Calculated from data in ^c Reference 35.	rwise stated. ref. 17.		

TABLE 6. α for reaction of 9-aryl-9-fluorenyl cations with water

Substit- uent	ΔG^{*a}	ΔG^{0}	α	pK _R ⁺
p-OMe	17.7	10.43	0.709	-7.64
p-Me	20.1	12.87	0.735	-9.43
н	21.5	14.76	0.761	-10.82
<i>m</i> -OMe	21.5	15.16	0.772	-11.11
m-Cl	23.2	17.19	0.794	-12.60
	Substit- uent p-OMe p-Me H m-OMe m-Cl	Substituent ΔG^{*a} p-OMe 17.7 p-Me 20.1 H 21.5 m-OMe 21.5 m-Cl 23.2	Substituent ΔG^{*a} ΔG^{0} p-OMe17.710.43p-Me20.112.87H21.514.76m-OMe21.515.16m-Cl23.217.19	Substituentuent ΔG^{*a} ΔG^{0} α p-OMe17.710.430.709p-Me20.112.870.735H21.514.760.761m-OMe21.515.160.772m-Cl23.217.190.794



Can. J. Chem. Downloaded from www.nrcresearchpress.com by ARIZONA STATE UNIVERSITY on 11/10/14 For personal use only.



FIG. 4. Plot of α against ΔG^{0} for the 9-aryl-9-fluorenyl cations.

results, we plotted α vs. ΔG^0 (Table 6 from the pK_{R+} values in Table 2) for the 9-arylfluorenols and obtained a linear plot (Fig. 4) with a correlation coefficient of 0.996. The ΔG^{\pm} values for the calculation of α were obtained from the kinetic data of Bolton et al. (15) and are referred to a different solvent system (9:1 ethanolacetone). However, to calculate α for our solvent system, a constant difference in ΔG^0 would be

involved and would not change the linearity of the plot.

While the parameter α is certainly an approximation, its linearity with pK (which must be limited as α approaches zero or unity) would seem to explain the success of the Hammett equation in the face of the apparently contradicting Hammond postulate. α also provides a simple method of converting equilibrium data into rate data, once the relationship between α and pK is established for a particular series.

The authors would like to thank the National Research Council of Canada for continued financial support.

- 1. G. A. OLAH. Acc. Chem. Res. 4, 240 (1971); J. H. RIDD. Acc. Chem. Res. 4, 248 (1971).
- H. C. BROWN and Y. OKAMOTO. J. Am. Chem. Soc. 79, 1913 (1957)
- 3. P. B. D. DE LA MARE, J. Chem. Soc. 4450 (1954); V. GOLD and D. P. N. SATCHELL, J. Chem. Soc. 2743 (1956).
- N. C. DENO and W. L. EVANS. J. Am. Chem. Soc. 79, 4. 5804 (1957).
- Y. YUKAWA and Y. TSUNO. Bull. Chem. Soc. Japan 32, 960 (1959).
- C. D. JOHNSON. The Hammett equation. Cambridge University Press. 1973.
- G. S. HAMMOND. J. Am. Chem. Soc. 77, 334 (1955). 7
- L. M. STOCK and H. C. BROWN. Adv. Phys. Org. 8. Chem. 1, 35 (1963).
- N. C. DENO, P. T. GROVES, and G. SAINES. J. Am. Chem. Soc. 81, 5790 (1959).
- I. I. SCHUSTER, A. K. COLTER, and R. J. KURLAND. J. 10. Am. Chem. Soc. 90, 4679 (1968).
- C. D. JOHNSON, A. R. KATRITZKY, and S. A. 11. SHAPIRO. J. Am. Chem. Soc. 91, 6654 (1969).
- M. J. COOK, N. L. DASSANAYAKA, C. D. JOHNSON, A. R. KATRITZKY, and T. W. TOONE. To be published.
- 13. D. G. LEE and R. CAMERON. J. Am. Chem. Soc. 93, 4724 (1971).
- C. EABORN, R. C. GOLESWORTHY, and M. N. LILLY. J. Chem. Soc. 3052 (1961).
- R. BOLTON, N. B. CHAPMAN, and J. SHORTER. J. Chem. Soc. 1895 (1964).
- 16 E. M. ARNETT. Prog. Phys. Org. Chem. 1, 223 (1963); M. A. PAUL and F. A. LONG. Chem. Rev. 57, 1 (1957).
- R. G. PEARSON and R. L. DILLON. J. Am. Chem. Soc. 75, 2439 (1953).
- J. R. JONES. Prog. Phys. Org. Chem. 9, 241 (1972). 18.
- R. A. DIFFENBACH, K. SANO, and R. W. TAFT. J. Am. 19. Chem. Soc. 88, 4747 (1966).
- 20. M. GOMBERG and C. C. BUCHLER. J. Am. Chem. Soc. 45, 207 (1923).
- 21. C. L. ARCUS and M. M. COOMBS. J. Chem. Soc. 3977 (1954).
- F. F. BLICKE and O. J. WEINHAUFF. J. Am. Chem. Soc. 54, 1460 (1932).
- 23. E. DE BARNETT and J. W. COOK. J. Chem. Soc. 2631 (1923).

- 24. K. YATES and R. A. MCCLELLAND. J. Am. Chem. Soc. 89, 2686 (1967).
- A. R. KATRITZKY. A. J. WARING, and K. YATES, Tetrahedron, 19, 465 (1963).
- 26. W. N. WHITE and C. A. STOUT. J. Org. Chem. 27, 2915 (1962).
- 27. N. C. DENO, J. J. JARUZELSKI, and A. SCHRIESHEIM. J. Am. Chem. Soc. 77, 3044 (1955).
- 28. A. C. NIXON and G. E. K. BRANCH. J. Am. Chem. Soc. 58, 492 (1936).
- E. D. HUGHES, C. K. INGOLD, and N. A. TAHER. J. Chem. Soc. 949 (1940).

Can. J. Chem. Downloaded from www.nrcresearchpress.com by ARIZONA STATE UNIVERSITY on 11/10/14 For personal use only.

Ö

- J. F. NORRIS and C. BANTA. J. Am. Chem. Soc. 50, 1804 (1928).
- 31. S. ALTSCHER, R. BALTZLY, and S. W. BLACKMAN, J. Am. Chem. Soc. 74, 3649 (1952).
- J. C. MARTIN and R. G. SMITH. J. Am. Chem. Soc. 86, 2252 (1964).
 R. A. DIFFENBACH. Ph.D. Thesis, Pennsylvania State
- R. A. DIFFENBACH. Ph.D. Thesis, Pennsylvania State U. 1968.
- N. C. DENO, J. J. JARUZELSKI, and A. SCHRIESHEIM. J. Org. Chem. 19, 155 (1954).
- 35. J. ARMAND and P. SOUCHAY. C. R. 225, 2112 (1962).