References and Notes

(1) G. P. Smith and R. N. Zare, *J. Am. Chem. Soc.*, **97**, 1985 (1975).
(2) D. J. Wren and M. Menzinger, *Chem. Phys. Lett.*, **27**, 572 (1974).
(3) C. D. Jonah, R. N. Zare, and Ch. Ottinger, *J. Chem. Phys.*, **56**, 263 (1972), report a total cross section of 27 $Å^2$ for the Ba + N_2O reaction.
(4) (a) C. A. Mims, Ph.D. Thesis, University of California, Berkeley (1973); (b) R. R. Herm, S.-M. Lin, and C. A. Mims, *J. Phys. Chem.*, **77**, 2931 (1973).
(5) The Ba + SO_2 product distribution reported in ref 4a was tentative because of an anomalously high background pressure during the experiment ($\sim 6 \times 10^{-6}$ Torr compared to $\lesssim 1 \times 10^{-6}$ Torr typical as measured by an ion gauge tube partially shielded from the BIR by an LN_2-cooled wall). Reference 4a argues that the detected BaO signal was not produced directly by reaction of Ba with this background SO_2. Nevertheless, a number of second-order effects associated with this limited SO_2 pumping capacity could have distorted the BaO product signal, e.g., BaO accumulation in the Ba primary beam due to reaction with SO_2 background which would then scatter elastically off of the modulated SO_2 beam. Because of these uncertainties, the BaO distribution was only alluded to as a tentative result in the publication based on this thesis work, ref 4b.
(6) J. C. Tully, *J. Chem. Phys.*, **61**, 61 (1974).
(7) G. E. Zahr, R. K. Preston, and W. H. Miller, *J. Chem. Phys.*, **62**, 1127 (1975).

R. Behrens, Jr., A. Freedman, R. R. Herm,* T. P. Parr

Ames Laboratory—ERDA and Department of Chemistry
Iowa State University
Ames, Iowa 50011

Received August 15, 1975

Aromatic Substitution, XXXIX.[1] Varying Selectivity in Electrophilic Formylation of Toluene and Benzene

Sir:

Electrophilic aromatic acylations (Friedel–Crafts ketone syntheses) generally show high substrate and positional selectivity,[2] with predominant para substitution of toluene.[2] Friedel–Crafts type formylation reactions, such as the Gatterman–Koch reaction, also give nearly exclusive para substitution.[3]

In the preceding study of aromatic substitution, we have reported the observation of the fairly wide scope of selectivity obtainable in electrophilic acetylation and benzoylation reactions of aromatics with suitable substituted acyl halides.[4] In the case of formylation, of course, no substituent effects are possible in the formylating agent, but the nature of the formylating agent can be easily varied.

We now wish to report our studies of electrophilic formylation of benzene and toluene, showing the wide range of selectivity obtainable depending on the used formylating agents.

From the most frequently used formylation methods, the Gatterman–Koch reaction[5] shows the highest selectivity (data are summarized in Table I) reflected both in the observed high $k_{toluene}:k_{benzene}$ rate ratios (of 155–860), as well as a high degree of para substitution (88.7–96%). Gross's formylation with dichloromethyl methyl ether[6] is somewhat less selective (k_T/k_B = 119; 60.4% para substitution), as is the Gatterman synthesis using $Zn(CN)_2$ and $AlCl_3$.[5] Friedel–Crafts type formylation with formyl fluoride[7] (the so-called Olah aldehyde synthesis[8]) gives a much lower selectivity ($k_T:k_B$ = 34.6 and 53% para substitution) indicating that the HCOF–BF_3 system produces a more reactive electrophile (HCOF·BF_3 complex, but not necessarily a free formyl cation, HCO^+).

The lowest selectivity reaction studied was the HF–SbF_5 catalyzed formylation with CO in SO_2ClF solution at −95°, which gave a k_T/k_B ratio of 1.6, and an isomer distribution of 45% *o*-, 2.7% *m*-, and 52.1% *p*-tolualdehyde. Under the superacidic conditions studied, CO is protonated to give the rapidly equilibrating (with the solvent acid system) protosolvated formyl cation, an obviously very reactive electrophilic reagent. When the reaction is carried out at 0 °C using only excess aromatics as solvent, the selectivity becomes much higher giving an isomer distribution of 7.5% *o*-, 2.8% *m*-, and 89.8% *p*-tolualdehyde.

The formylation of hexadeuteriobenzene, C_6D_6, with HCOF–BF_3 shows a kinetic hydrogen isotope effect of k_H/k_D = 2.68, based on the comparison of the reactivity of $C_6H_6/CH_3C_6H_5$ and $C_6D_6/CH_3C_6H_5$. This isotope effect is similar to that observed in Friedel–Crafts acetylation and propionylation reactions, and indicates that the proton elimination step is at least partially rate determining. The low substrate selectivity formylation with CO–HF–SbF_5, however, shows no primary isotope effect.

For nearly a century Friedel–Crafts acylations were considered to give nearly exclusive para substitution of toluene.[2] The reason accounting for this fact was considered to be steric. Our increasingly better understanding of the mechanism of electrophilic aromatic substitution indicated that this is not necessarily the only reason. Para substitution is greatly favored if the transition state of highest energy of the reaction is intermediate arenium ion (σ-complex) like, where a para methyl group is more stabilizing than an ortho (and much more than a meta). When, however, the highest transition state is becoming increasingly "early" on the reaction path, the ratio of ortho/para substitution increases. Meta substitution always stays relatively low, generally less than 5–6%, varying with the reactivity of the reagent within this limit. It is rewarding to see this pattern now also in Friedel–Crafts type formylation reactions. In these reactions the involved substituting agents are obviously less space demanding than those of other acylation reactions. Steric effects consequently cannot be a very significant factor affecting selectivity, which is primarily reflected in the changing ortho/para isomer ratio. The methyl group always remains a predominately ortho–para directing substituent, even in very low substrate selectivity reactions and the meta isomer does not increase above 4%.

Besides mechanistic interest, our studies are also considered to eventually contribute to the extended preparative usefulness of Friedel–Crafts syntheses in obtaining previously not easily accessible isomers (such as *o*-tolualdehyde). Our studies are extended to the formylation of other substituted aromatics, and will be reported in full.

Table I. Electrophilic Formylation of Toluene and Benzene

Formylating agent	Catalyst	Solvent	Temp, °C	k_T/k_B	% tolualdehydes		
					Ortho	Meta	Para
CO	HF–SbF_5	SO_2ClF	−95	1.6	45.2	2.7	52.1
HCOF	BF_3	Excess aromatics	25	34.6	43.3	3.5	53.2
HCN–HCl	$AlCl_3$	Excess aromatics	25	49.1	39.9	3.7	56.4
$Zn(CN)_2$–HCl	$AlCl_3$	CH_3NO_2	25	92.8	38.7	3.5	57.8
$Zn(CN)_2$–HCl	$AlCl_3$	Excess aromatics	50	128	34.3	1.8	63.9
Cl_2CHOCH_3	$AlCl_3$	CH_3NO_2	25	119	35.8	3.8	60.4
CO + HCl	$AlCl_3Cu_2Cl_2$	Excess aromatics	25	155	8.6	2.7	88.7
CO + HCl	$AlCl_3$	Excess aromatics	0	319	6.6	0.8	92.6
CO + HF	BF_3	Excess aromatics	0	860	3.5	0.5	96.0

Acknowledgment. Support of our work by the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

References and Notes

(1) Part XXXIX. G. A. Olah, D. A. Beal, and J. A. Olah, *J. Org. Chem.*, in press.
(2) G. A. Olah, "Friedel-Crafts Chemistry", Wiley-Interscience, New York, N.Y., 1973, and references therein.
(3) N. N. Grounse, *Org. React.* **5**, 290 (1949), and references therein.
(4) G. A. Olah and S. Kobayashi, *J. Am. Chem. Soc.*, **93**, 6964 (1971).
(5) For a review see G. A. Olah and S. J. Kuhn in "Friedel-Crafts and Related Reactions", Vol. III, G. A. Olah, Ed., Wiley-Interscience, New York, N.Y., 1964, pp 1153.
(6) (a) A. Rieche, H. Gross, and E. Höft, *Chem. Ber*, **93**, 88 (1960); (b) ref 4, pp 1189.
(7) G. A. Olah and S. Kuhn, *Chem. Ber*, **89**, 866 (1956); *J. Am. Chem. Soc.*, **82**, 2380 (1961).
(8) H. R. Christen "Grundlagen der Organische Chemie", Verlag Sauerlander-Diesterweg, Aarau-Frankfurt am Main, 1970, pp 242.
(9) Visiting Scientist from Societa Italiana Resine, Milano, Italy.
(10) Postdoctoral Research Associate from Kyoto University, Japan.

George A. Olah,* Franco Pelizza[9]
Shiro Kobayashi,[10] Judith A. Olah
Department of Chemistry, Case Western Reserve University
Cleveland, Ohio 44106
Received August 26, 1975

Cyclopropanation Transition States. The Electronic Effect

Sir:

The stereochemistry of olefin cyclopropanation by carbenes and carbenoids has been a particularly active topic for the past several years.[1] Possible influences include electronic effects,[1,2] steric effects,[1b] and specific complexation effects involving metal ions[3] or substituted olefins.[4] Electronic effects have been attributed to dispersion forces,[5] secondary electrostatic interactions,[6,7] or, more generally, secondary electronic interactions viewed in molecular orbital terms.[8] These suggestions are based on experiments involving unsymmetrical carbenes or carbenoids in which the two groups differ in size as well as electronics. Only if one assumes a very early transition state, can steric differences be ignored. Such an assumption is probably justified in Closs's substituent work on the reactive monoarylcarbenes[6] and monoarylcarbenoids,[6,9] but the endo-aryl and endo-hydrogen transition states probably occur at different separation distances which could change electronic effect magnitudes.

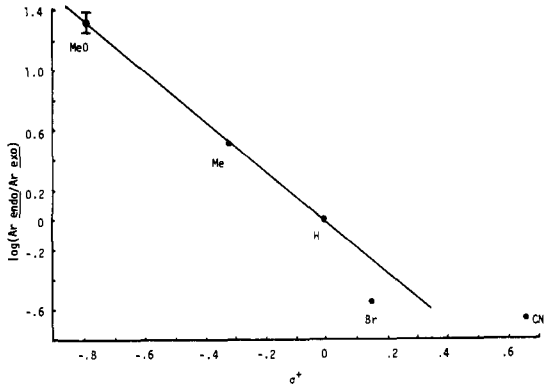
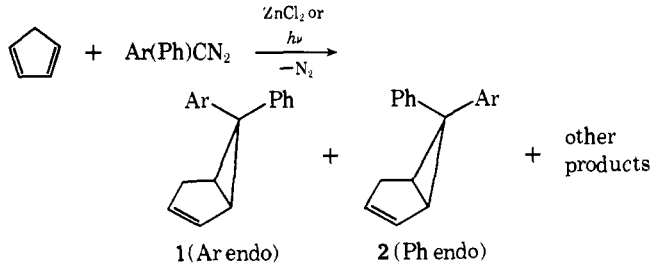


Figure 1. σ^+ ρ plot of diarylcarbenoid cyclopropanation stereoselectivity at 0 °C.

We felt that examining the effect of para substitution on diarylcarbenoid and diarylcarbene cyclopropanations would clarify the electronic effect since the transition states leading to **1** (Ar endo) and **2** (Ph endo) should occur at the same carbene-olefin separation distance and would therefore have the same steric hindrance between the endo-group and the olefin substrate. Furthermore, the low reactivity of



the diaryl species implies a relatively product-like transition state with only small carbene-olefin separation[10] where both steric and electronic effects might be maximized. The appropriate diaryldiazomethanes were added to cyclopentadiene in the usual fashion[11] using both zinc chloride catalysis and Pyrex filtered irradiation. Reverse-phase high pressure liquid chromatography[12] allows analytical separation of the isomeric olefin products[13] without fear of isomerization so that reliable kinetic stereoselectivities can be obtained. The stereochemistry of the 6,6-diarylbicyclo[3.1.0]hex-2-enes (**1**) and (**2**) can be determined by application of europium shift reagents[14,15] to the hydroboration derived 6,6-diarylbicyclo[3.1.0]hexan-3-*exo*-ols.

The results for both the carbene and carbenoid reactions are shown in Table I. Note that in all cases the major prod-

Table I. Substituent Effects on Diarylcarbene and Diarylcarbenoid Reactions

$Ar(Ph)CN_2$	Conditions (°C)	Cyclopropane	Ar_{endo}/Ar_{exo}[a]	Benzophenone	Ketazine[b]
p-C_6H_4CN	$ZnCl_2$ (25)	37	1/2.5	15	35
	$ZnCl_2$ (0–5)	9	1/4.5	20	50
	$h\nu$ (0–5)	32	1/3.2	20	4 (24)[c]
p-C_6H_4Br	$ZnCl_2$ (25)	31	1/3.5	68	5
	$ZnCl_2$ (0–5)	21	1/3.6	17	24
	$h\nu$ (0–5)	25	1/3.5	26	— —(25)[c]
Ph[d]	$ZnCl_2$ (25)	35	— —	29	24
Ph[d]	$ZnCl_2$ (0–5)	23	— —	15	51
Ph[d]	$h\nu$ (0–5)	19	— —	25	1 (36)[c]
p-$C_6H_4CH_3$	$ZnCl_2$ (25)	12	2/1	5	60
	$ZnCl_2$ (0–5)	20	3/1	24	25
	$h\nu$ (0–5)	14	1.1/1	35	20 (10)[c]
p-$C_6H_4OCH_3$	$ZnCl_2$ (25)	11	≥20/1[e]	46	10
	$ZnCl_2$ (0–5)	5	≥20/1[e]	47	30
	$h\nu$ (0–5)	15	≥20/1[e]	21	(22)[c]

[a] Isomer ratio determined by recycling reversed phase HPLC with 254-nm detector. [b] Ketazine = tetraarylketazine. [c] Yield of 1,1,2,2,-tetraarylethane. [d] From ref 8. [e] No second isomer could be seen by NMR or recycling HPLC on the crystalline isomer mother liquors. We estimate a maximum of 5% of a second isomer could be present.