nitro chromium acetylacetonate is a manifestation of steric inhibition of resonance of the nitro group with the chelate ring. In the case of the nitro chelates III and IV the nitro groups can become coplanar with the chelate ring as is indicated by a bathochromic shift of about 20 mμ; whereas in the nitro-acetylacetonate the nitro groups probably are forced out of the plane of the chelate ring by the two flanking methyl groups. The bromine atom, being spherical, gives rise to a bathochromic shift in all three cases. The short wave length bands are used in this argument.

TABLE I

ULTRAVIOLET SPECTRA OF METAL CHELATES

R	R'	X	CHCl₃, λ_{max}	ϵ
CH₃	CH₃	H	335	15,800
CH₃	CH₃	Br	358	13,070
CH₃	H	NO₂	330	12,260
CH₃	H	H	259	9,950
			275	9,400
			301	7,980
			337	13,040
CH₃	H	Br	277	8,710
CH₃	H	NO₂	282	27,250
			319	14,650
H	H	H	265	8,580
			341	10,850
H	H	NO₂	282	31,000
			322	12,500

Work is in progress on further electrophilic substitutions of these new chelate rings, and on the reactions of functional groups substituted on these rings.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NORTH CAROLINA   JAMES P. COLLMAN
CHAPEL HILL, N. C.   EDMUND T. KITTLEMAN
            RECEIVED JULY 17, 1961

THE MECHANISM OF THE REACTION OF GRIGNARD REAGENTS WITH SCHIFF BASES

Sir:

Although several kinetic investigations of Grignard reactions have been made[1-7] none of them has involved systems in which the Grignard reagent added across an unsaturated linkage capable of being substituted at both ends. Data on such a reaction would clearly provide a keener insight into the behavior of organomagnesium compounds.

It is well known that Schiff bases, RCH=NR', react conveniently with "R''MgX" yielding

(1) D. Ivanoff and J. Abduloff, Compt. rend., 196, 491 (1933).
(2) H. Kleinfeller and H. Lohman, Ber., 71, 2608 (1938).
(3) C. G. Swain, J. Am. Chem. Soc., 69, 2307 (1947).
(4) J. Aston and S. Bernhard, Nature, 165, 485 (1950).
(5) A. Bruylants, Bull. Soc. Chim. France, 1958, 1291.
(6) S. J. Storfer and E. J. Becker, personal communication.
(7) R. E. Dessy, J. H. Wotiz and C. A. Hollingsworth, J. Am. Chem. Soc., 79, 358 (1957).

halomagnesium salts of amines according to the equation[8]

$$RCH=NR' + \text{``R''MgX''} \xrightarrow{Et_2O} RR''CH-NR'(MgX) \quad (1)$$
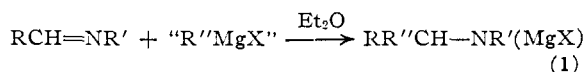
Using the change in dielectric constant of the reaction mass as function of time as a tool[9] to follow the rate of reaction of various Schiff bases with ethylmagnesium bromide we have been able to provide such data.

The literature[8] reports that yields of amines in this reaction are less than 50% when a 1:1 ratio of "RMgX"/Schiff base is employed, although quantitative yields may be obtained when 2/1 ratios are employed.

Employing gas chromatography as an analytical tool we have found that reaction of benzalaniline with ethylmagnesium bromide gives N-α-phenylpropylaniline in 50% yields when a 1/1 ratio of "RMgX"/Schiff base is employed. 100% yields (based on Schiff base) are found at 2/1 ratios.

This suggests that only one-half of the available R groups are utilized in the addition of a Grignard reagent across the azomethine link of Schiff bases, and agrees with the work of Becker[7,10] on the reaction of benzonitrile with Grignard reagents, in which the same phenomenon was noticed. Such a fact is explained easily if one accepts that a Grignard reagent is more accurately portrayed as $R_2Mg\cdot MgX_2$ than $RMgX$[11].

Addition of one of the R–Mg linkages across the azomethine link leads to a product in which reaction of the second R–Mg linkage is prevented by steric or electronic factors.
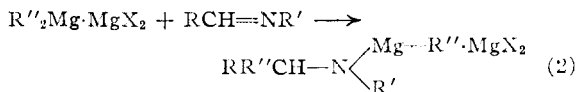
$$R''_2Mg\cdot MgX_2 + RCH=NR' \longrightarrow$$
$$RR''CH-N\begin{array}{c}Mg-R''\cdot MgX_2\\R'\end{array} \quad (2)$$

Table I shows the results obtained when various substituents were placed on the rings of benzalaniline.

TABLE I

$$\text{``EtMgBr''} + Z-C_6H_5CH=N-C_6H_5Z' \xrightarrow{Et_2O} \\ 31.5°$$

Z	Z'	Schiff base molarity	"EtMgBr" molarity	k,[a] 1./ mole-sec. $\times 10^4$
H	H	0.30	0.15	2.3
H	H	.20	.20	2.7
H	H	.15	.20	2.7
p-CH₃O	H	.20	.20	2.8
H	p-CH₃O	.20	.20	1.4
H	p-Cl	.20	.20	2.3

[a] Rate = $k(Et_2Mg\cdot MgBr_2)(\text{Schiff Base})$.

Several kinetic expressions were tested: rate = $k(\text{``EtMgBr''})$, rate = $k(\text{``EtMgBr''})(\text{Schiff base})$, and rate = $k(Et_2Mg.MgBr_2)(\text{Schiff base})$. Only the last of these gave good kinetic plots and consistent k's, as Table I indicates.

(8) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice Hall, New York, N. Y., 1954.
(9) R. E. Dessy and R. M. Salinger, J. Org. Chem., in press.
(10) S. J. Storfer and E. J. Becker, Abstracts, 138th meeting of Am. Chem. Soc., Sept. 11-16, 1960, New York, p. 80-P.
(11) R. E. Dessy and G. S. Handler, J. Am. Chem. Soc., 80, 5824 (1958).

If preferential attack at C or N occurred, substitution in either ring should affect the rate of reaction—similarly, if complexing of the Grignard reagent with the azomethine link was rate determining, substitution should affect the observed rate. This clearly is not the case. The data do suggest a four-center mechanism for the reaction.

>C=N⁻   ⟶   >C=N—   ⟶   >C—N⁻
R—Mg⌐   ⟵   R---Mg⌐   R Mg⌐
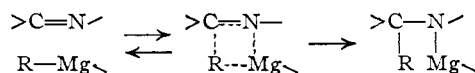
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CINCINNATI   RAYMOND E. DESSY
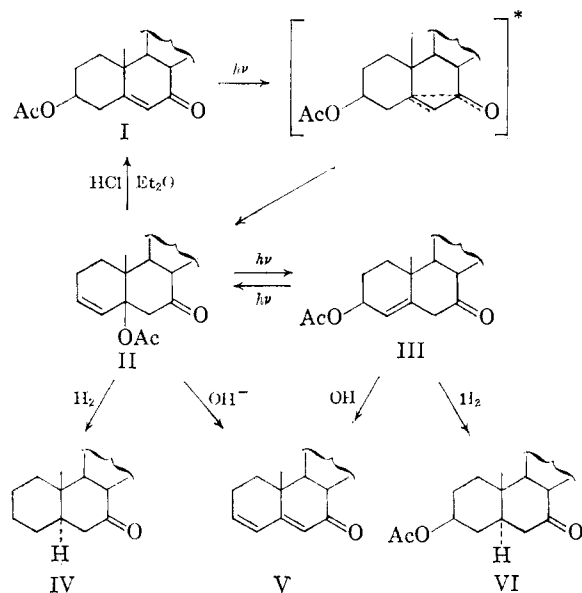CINCINNATI 21, OHIO   RUDOLF M. SALINGER
              RECEIVED JUNE 3, 1961

A PHOTOCHEMICAL ESTER REARRANGEMENT INDUCED BY HOMOCONJUGATION EXCITATION[1]

Sir:

It has long been recognized that certain types of non-conjugated unsaturated ketones exhibit enhanced ultraviolet absorption in the 270–310 mμ region (n → π^* transition).[2] Only recently have the orbital geometry requirements for this phenomenon been understood.[3,4,5] The interesting question now posed is whether or not this mode of excitation of a double bond will give rise to chemical reaction. The report of such a reaction is the content of this communication.

The irradiation[6] of 7-ketocholesteryl acetate (I) afforded two photo products which, by chromatography, were easily separated from each other and from starting material. One of these, 5β-acetoxy-
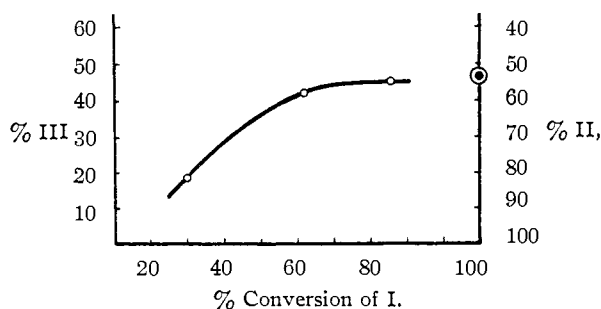

Fig. 1.—Results of irradiation of I for varying periods of time. Data expressed represent the isolated quantities of II and III. The solid circle indicates the equilibrium value established independently from pure II and pure III.

cholest-3-ene-7-one (II), had m.p. 114.0–114.5°, λ_{max}^{EtOH} 280 mμ, ϵ 77, $[\alpha]_D^{22}$ + 33 (CHCl₃) and was shown to be isomeric with I (Found: C, 78.70; H, 10.43). Infrared absorption at 5.81, 5.86 and 6.06 μ suggested II to be an unsaturated ketol acetate. Hydrogenation (Pd–C, ethanol) required 2.07 mole-equivalents of hydrogen and afforded 7-cholestanone (IV), identified by the usual comparisons with an authentic sample.[7] Treatment of II with methanolic potassium hydroxide gave rise to 3,5-cholestadien-7-one (V), identical in all respects with authentic material. The same transformation was effected by refluxing II in a solution of sodium acetate in acetic acid or by heating a sample above its melting point. The isomerization of II back to I occurred readily when a sample dissolved in ether was saturated with dry hydrogen chloride. These data are consistent with the assignment of structure shown in II. The configuration about C-5 was not established rigorously but must be as shown to accommodate the stereospecificity observed in the interconversion of II and III as well as in the isomerization of II to I.

The second photo compound, 3β-acetoxycholest-4-ene-7-one (III), m.p. 151–153°, λ_{max}^{EtOH} 284, ϵ, 86, $[\alpha]_D^{22}$ +35 (CHCl₃) (Found: C, 78.80; H, 10.31) is formulated as shown from the fact that it gave 7-ketocholestanyl acetate (VI) upon catalytic hydrogenation. Like II, it afforded the dienone (V) upon treatment with base.

The sequential order of formation of II and III was established with data taken from several runs in which the irradiation time was varied so as to give conversions of I ranging from 20% to 76%. They are summarized in Fig. 1. It seems clear that II is the primary product and that III is formed from II. The irradiation of pure samples of either II or III gave an equilibrium mixture of the two. It is significant that not even traces of I could be detected during the careful chromatographic analysis of these mixtures; I appears not to be an equilibrium component.

The nature of the excited state linking I and II cannot be described with any certainty. The degree of stereospecificity observed suggests that the process involves "cart-wheeling" of acetoxyl with

(1) Supported by the National Institutes of Health (Grant RG-7861).

(2) See for example P. D. Bartlett and B. E. Tate, J. Am. Chem. Soc., **78**, 2473 (1956).

(3) S. Winstein, L. de Vries and R. Orloski, ibid., **83**, 2020 (1961), and references cited therein.

(4) R. C. Cookson, R. R. Hill and J. Hudec, Chem. & Ind., 589 (1961).

(5) E. M. Kosower, W. D. Closson, H. L. Goering and J. C. Gross, J. Am. Chem. Soc., **83**, 2013 (1961).

(6) All irradiation experiments were conducted using a 200-w. high-pressure mercury vapor lamp positioned internally in a t-butyl alcohol solution of the reactant; a 2 mm. Pyrex filter was employed.

(7) The stereochemical course of this hydrogenolysis is analogous to that observed with verbesinol, P. D. Gardner, G. J. Park and C. C. Albers, J. Am. Chem. Soc., **83**, 1511 (1961), and will be discussed in the complete article.