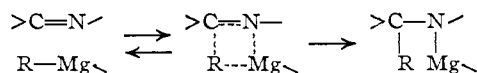If preferential attack at C or N occurred, substitution in either ring should affect the rate of reaction—similarly, if complexing of the Grignard reagent with the azomethine link was rate determining, substitution should affect the observed rate. This clearly is not the case. The data do suggest a four-center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

$$>C=N\diagdown \underset{R—Mg\diagdown}{\overset{\longrightarrow}{\longleftarrow}} \overset{>C=N—}{R---Mg\diagdown} \longrightarrow \overset{>C—N\diagdown}{R \quad Mg\diagdown}$$

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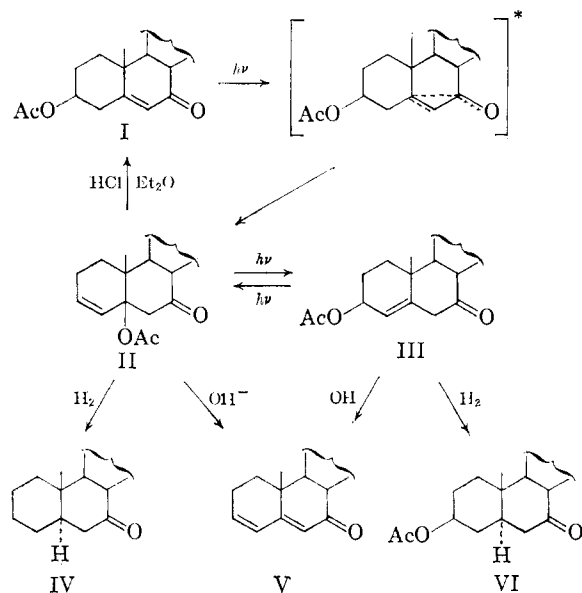
(1) Supported by the National Institutes of Health (Grant RG-7861).

(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.
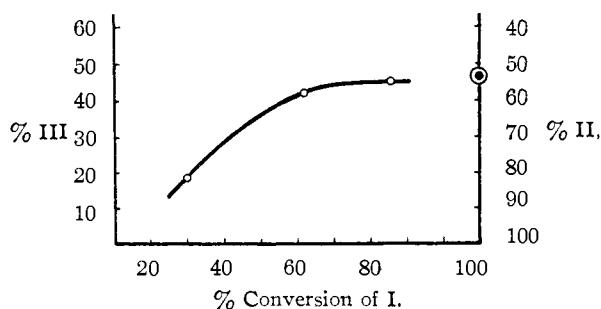

Fig. 1.—Results of irradiation of I for varying periods of time. Data expressed represent the isolated quantities of II and III. The solid circle indicates the equilibrium value established independently from pure II and pure III.

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

(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.

or without charge-separation.[8] The excited state linking II and III, on the other hand, must be charge-separated. The only ultraviolet absorption exhibited by these substances above 220 mμ is the n $\rightarrow$ π^* band in the 280 mμ region and the rather large extinction coefficients observed indicate considerable interaction in the excited state between the carbonyl group (ketone) and the double bond.[3,5] This is a result of the favorable orbital overlap imposed by the rigidity of II and III and is possible in II because of the cis ring fusion.

The possibility that the rearrangement is the result of normal excitation (singlet) of the ketone carbonyl followed by an internal transfer of energy to the reaction site cannot be discarded. It seems unlikely, however, as an indiscriminate transfer of energy to ring-A would be expected to induce elimination of acetic acid and give rise to the dienone (V) or ultimately to its photodimer (a high-melting solid). Neither could be isolated. Experiments designed to establish this important point in an unequivocal manner are in progress.

The irradiation of trans-cinnamyl acetate gave no evidence of acetate migration but instead afforded a dimeric product which appears to be a substituted cyclobutane.

(8) Such a mechanism appears to operate in a type of 1–2 acetate rearrangement, D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959).

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STERIC EFFECTS ON NITROGEN HYPERFINE COUPLING IN METHYL SUBSTITUTED MONO- AND DINITROBENZENE ANION RADICALS

Sir:

The recent electron spin resonance (e.s.r.) study of an extensive series of para substituted nitrobenzene anion radicals has established the dependence of the nitrogen hyperfine coupling constant on the inductive and mesomeric nature of the para substituent.[1] We now wish to report hyperfine coupling data for a series of methyl substituted nitrobenzene anion radicals.

Comparison of the nitrogen coupling constant, $|a_N|$, for the anion radicals of nitrobenzene (10.32 gauss), 1,3-dimethyl-2-nitrobenzene (17.8 gauss), and 2,3,5,6-tetramethylnitrobenzene (20.4 gauss) establishes clear evidence of sterically-induced decoupling of the nitro group π-electron system from the aromatic π-electron system. Analogous evidence is available for dinitrobenzene anion radicals. Maki and Geske[2] have suggested previously that the unusually low nitrogen coupling constant for the anion radical of p-dinitrobenzene (1.74 gauss) could be accounted for on the basis of significant mesomeric interaction between the two nitro groups. It is therefore significant that the nitrogen coupling constant for the anion radical of the totally methylated derivative, 1,4-dinitrodurene, is increased to 8.7 gauss.

The data presented in Table I suggest that the inductive effect of the methyl group is not of

(1) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).
(2) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).

importance in determining the gross trend observed in the distribution of spin density in this series of radicals. The comparatively small effect on $|a_N|$ of introducing a single ortho-methyl group as compared to di-ortho substitution parallels other chemical observations.[3] It is apparent from the decrease of all ring coupling constants simultaneously with an increase in the nitrogen coupling constant that the net result of steric interference by ortho methyl groups is to localize more and more of the odd electron density on the nitro group to the exclusion of the ring. In this light it is significant that $|a_N|$ observed for the highly hindered compounds approaches the nitrogen coupling constant for various nitroaliphatic anion radicals, 22.9–25.2 gauss.[4] Successful observation of nitroaliphatic anion radicals demonstrates that the stabilizing influence of the aromatic ring, while considerable, is not necessary to the existence of nitro anion radicals.

TABLE I

COUPLING CONSTANTS FOR ANION RADICALS OF METHYL SUBSTITUTED NITROBENZENES

Methyl position[b]	Coupling constants[a] (absolute value in gauss)			
	a_N	a_o	a_m	a_p
. . .[c]	10.32	3.39	1.09	3.97
4[c]	10.79	3.39	1.11	3.98
3,5	10.6	3.29	1.08	3.92
2	11.0	3.12	1.04	3.91
2,3	11.7	2.91	0.99	3.3
2,6	17.8	0.87	. . .[d]	1.44
2,3,5,6	20.4	. . .[d]	. . .[d]	. . .[d]

^{a} a_o, a_m and a_p are coupling constants for positions ortho, meta and para to nitro group. For a given position, ring protons and methyl group protons have identical coupling constants within the resolution of our assignments. ^{b} Nitro group assigned ring position 1. ^{c} Data from ref. 1. ^{d} No discrete structure was evident on these lines. In view of the known resolution of the instrument ($\leq$ 0.1 gauss), the coupling constant must be appreciably less than the observed line width of 1.2 gauss.

The trend observed in coupling constants is consistent with a qualitative explanation invoking twisting of the nitro group about an axis lying in the ring. Such a deformation would clearly reduce the coupling between the contiguous π-electron systems. A second possibility, that of deformation of the nitro group from coplanarity with the abutting carbon atom, would also increase the nitrogen coupling constant via the accompanying necessary increase in s-character of the nitrogen orbital involved in the nitro group π-electron system. This increase in s-character would increase the scale of the contact interaction without requiring an increase in spin density. However, for small distortions, it seems likely that the latter mechanism would produce only a slight effect on the coupling with the ring, and thus would not agree with the experimental observations.

E.s.r. data were obtained with an X-band homodyne balanced mixer spectrometer using bolometer detection and 400 cycle audio modulation. The anion radicals were generated electrolytically

(3) B. M. Wepster in "Progress in Stereochemistry," Vol. 2, edited by W. Klyne and P. B. D. de la Mare, Butterworths Scientific Publications, London, 1958, p. 99.
(4) L. Piette, P. Ludwig and R. N. Adams, private communication.