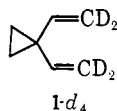isotope effect was taken as the rate ratio of $1/1\text{-}d_4$ at 242°:[4] $(k_H/k_D)_{inter} = 1.08 \pm 0.07$.

1-d_4

While the identity of the two secondary isotope effects *could* be interpreted as deriving from a common transition state for the rate-determining and the product-forming steps, and this may be equated with the process being concerted, we do *not* favor this explanation. Most importantly, the preponderant weight of analogy insists that a rate-determining process, in which an sp² carbon is transformed into an sp³ carbon, should be associated with an *inverse* kinetic secondary deuterium isotope effect.[9,11] It is difficult to conceive a single transition-state process which can simply account for the nature of the observed isotope effect. Nevertheless, due to a general paucity of isotope effect data for similar reactions, it is presently not possible to definitively rule out a concerted mechanism.

Presently, in light of all past analogy, we tend to favor the interpretation of the results as indicating a multistep process. In this case, there are two possible pathways, rate-determining diradical formation or rate-determining diradical destruction.

In the former situation, there is some analogy that a normal intermolecular isotope effect is to be expected for the conversion, sp² → radical,[13-15] in which case our observed intermolecular effect could derive from rate-determining formation of diradical 3, and our observed intramolecular effect, while being relatively small,[9,15] can be understood as deriving from the product-forming destruction.

In the latter situation, a preequilibrium formation of diradical 3 would result in the rate-determining and product-forming transition states being one and the same, and thus the two isotope effects should be near identical and resembling in value those ordinarily observed for diradical cyclizations.[9,15]

Secondary deuterium isotope effects have not generally been applied to mechanistic studies of thermal rearrangements. It is our feeling that they may indeed be useful in probing the intricacies of the energy surfaces of such reactions and may provide insight as to the relationships between diradicals generated from cycloaddition processes and these generated in thermal rearrangements. We are presently involved in further studies which we hope will increase our understanding of secondary deuterium isotope effects and enhance their viability as a probe in distinguishing one- and two-step mechanisms.

(11) The only possible exception to this general observation is the as·yet anomalous ketene–styrene [2 + 2] study of Baldwin.[12] It is difficult to relate his results to our work at present.

(12) J. E. Baldwin and J. A. Kapecki, *J. Amer. Chem. Soc.*, **91**, 3106 (1969).

(13) J. E. Baldwin and R. Fleming, *Fortsch. Chem. Fortsch.*, **15**, 281 (1970).

(14) W. A. Pryor and R. W. Henderson, *Int. J. Chem. Kinet.*, in press; we thank Professor Pryor for allowing us to read his manuscript prior to publication.

(15) S. H. Dai and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, in press.

William R. Dolbier, Jr.,*[16] Jorge H. Alonso[17]
Department of Chemistry, University of Florida
Gainesville, Florida 32601
Received December 23, 1971

## A New Type of Substitution at a Saturated Carbon Atom

Sir:

We describe a new type of substitution which occurs at a saturated carbon atom attached to the anthracene nucleus and which, presumably, will be observed with other polycyclic derivatives and related heterocycles.

Nitroparaffin salts ordinarily undergo oxygen alkylation on treatment with benzylic halides;[1] it is not surprising, then, that when 9-chloromethylanthracene (I) is treated with the lithium salt of 2-nitropropane (II) in hexamethylphosphoramide (HMPA) at 25° an 85% yield of 9-anthraldehyde (III) is obtained (eq 1). In

(1)
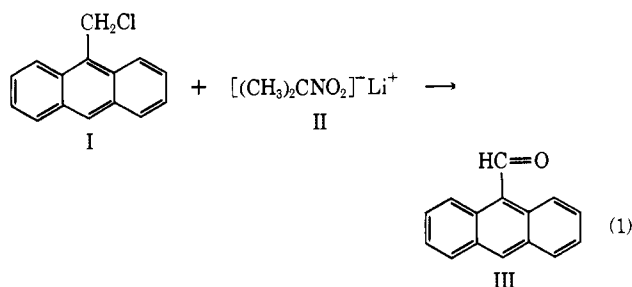
sharp contrast, when the quaternary ammonium salt IV reacts with the lithium salt of 2-nitropropane (II) a 90% yield of the pure carbon alkylate V is produced (eq 2).


(2)
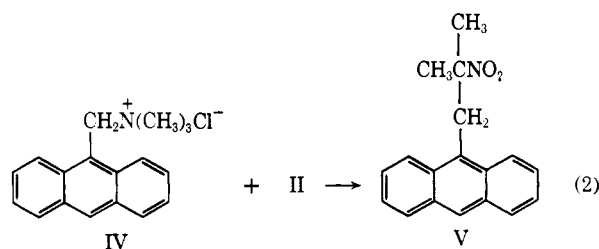
If the reaction of eq 2 is carried out using less than a stoichiometric amount of the nitroparaffin salt a new compound VI, isomeric with the carbon alkylate V, can be isolated;[2] this new compound is rapidly and quantitatively isomerized to V on treatment with the lithium salt of 2-nitropropane (eq 3) and clearly is an intermediate in the carbon alkylation reaction.

The isomerization process described by eq 3 is not intramolecular; for, if instead of II, the salt of 2-nitrobutane is used, then the alkylated 2-nitrobutane VII is obtained in 89% yield (eq 4). Thus, carbon alkylation (eq 2) occurs in stages: in the first the intermediate VI

(1) L. Weisler and R. W. Helmkamp, *J. Amer. Chem. Soc.*, **67**, 1167 (1945); H. B. Hass and M. L. Bender, *ibid.*, **71**, 3482 (1949).

(2) Satisfactory elemental analyses and nmr and ir spectra were obtained for all new compounds.

$$\text{VI} + \text{II} \longrightarrow \text{V} + \text{II} \qquad (3)$$
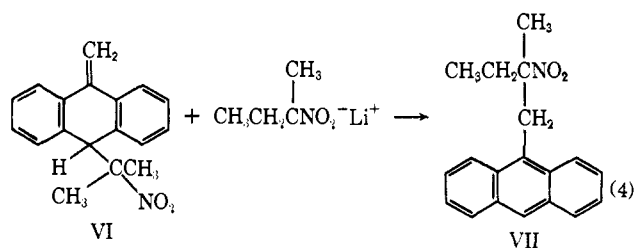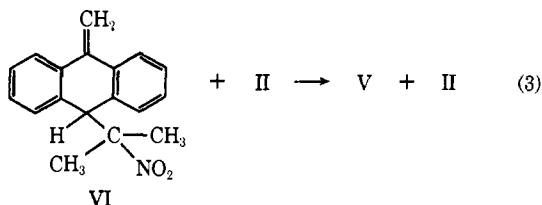
(eq 5) is produced and in the second this is transformed into the final product V (eq 3).

$$\text{IV} + \text{II} \longrightarrow \text{VI} + \text{N(CH}_3)_3 + \text{LiCl} \qquad (5)$$

Completely analogous results are obtained when the quaternary ammonium salt IV is treated with a 2-nitrobutane or nitrocyclohexane salt; the corresponding carbon alkylate, VII or VIII, is produced in 80–85% yield. Here, again, intermediates, IX and X, have been isolated, characterized,[2] and shown to isomerize rapidly
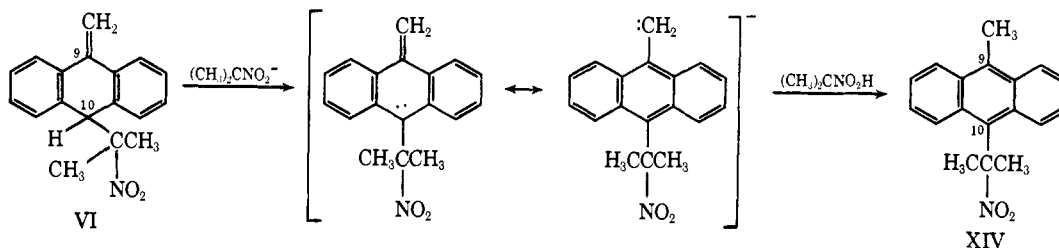

and quantitatively to the carbon alkylates VII and VIII when treated with the respective nitroparaffin salts.
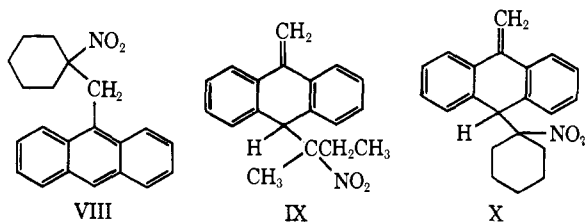
This novel type of substitution is not confined to reactions involving nitroparaffin salts. For example, 9-chloromethylanthracene (I) reacts rapidly at room temperature with the methylmalonic ester salt XI to give XII in greater than 90% yield (eq 6), and there is no reason to regard this as anything more than an S$_N$2 displacement. When the quaternary ammonium salt IV is treated with the methylmalonic ester salt XI the alkylate XII is again obtained (91% yield), but now the

$$(6)$$
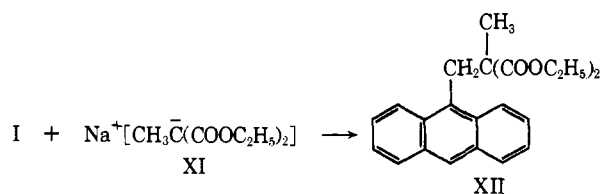
reaction is clearly something more than a simple S$_N$2 displacement; an intermediate, XIII,[2] is isolated which, on treatment with the methylmalonic ester salt XI in HMPA at 25°, readily isomerizes to XII. Thus, with the malonate anion, displacement of trimethylamine from IV is also a stepwise process (eq 7 and 8). In

$$(7)$$

$$\text{XIII} + \text{XI} \longrightarrow \text{XII} + \text{XI} \qquad (8)$$
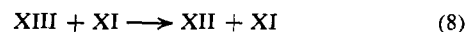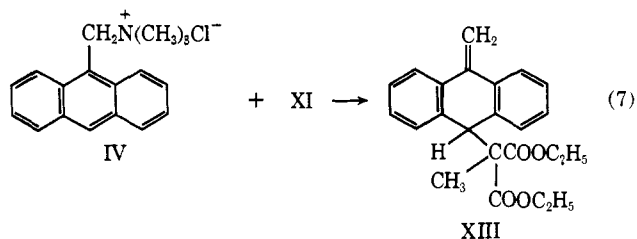
keeping with this view, when the methylmalonic ester intermediate XIII is treated with 10 equiv of the lithium salt of 2-nitropropane (II) at 25° a 91% yield of the pure 2-nitropropane alkylate (V) is obtained (eq 9).[3]

$$\text{XIII} + \text{II} \longrightarrow \text{V} \qquad (9)$$

In principle, the intermediates VI, IX, X, and XIII can undergo a prototropic shift under the basic reaction conditions to give the corresponding 9-methyl 10-substituted anthracenes, e.g., with VI

But, in actuality, the prototropic shift does not compete with the isomerization reaction of eq 3.

The ease with which the prototropic shift can occur is a function of the substituent at C-10 and in this connection studies employing sodium thiophenoxide are instructive. At 25°, in HMPA, sodium thiophenoxide and 9-chloromethylanthracene (I) give but a single product, XV, isolated in 96% yield (eq 10); here, again,

$$\text{I} + \text{Na}^+\bar{\text{S}}\text{C}_6\text{H}_5 \longrightarrow \qquad (10)$$
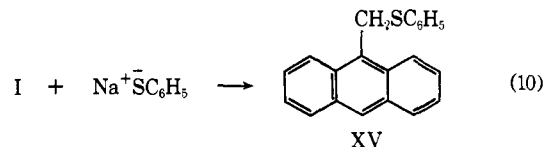
there is no reason to regard the reaction as anything but an S$_N$2 displacement. On the other hand, when the quaternary ammonium salt IV is treated with sodium thiophenoxide two products are obtained: XV in 62% yield and 9-methyl-10-thiophenoxyanthracene (XVI) in 26% yield (eq 11). Here again we deal with a multi-

$$\text{IV} + \text{Na}^+\bar{\text{S}}\text{C}_6\text{H}_5 \longrightarrow \text{XV} + \qquad (11)$$
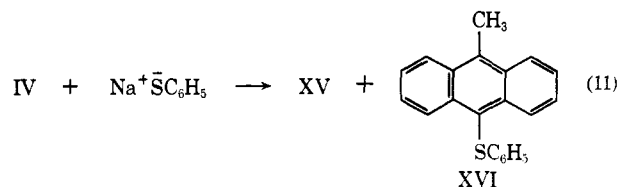
(3) As anticipated, XII is stable to II under these conditions.

stage process, but now the intermediate XVII, unlike the other intermediates, is able to undergo the prototropic shift productive of a 9-methylanthracene, presumably because the thiophenoxy group has a relatively small steric requirement and, also, because sulfide sulfur stabilizes a carbanion.[4,5]

Sodium thiophenoxide reacts with the quaternary ammonium salt IV much more rapidly than it does with benzyltrimethylammonium chloride (half-life of 3 min as opposed to 70 hr). Whereas the reaction of the lithium salt of 2-nitropropane with the quaternary ammonium salt IV (eq 2) is 50% complete in 1 hr there is no detectable reaction between the lithium salt of
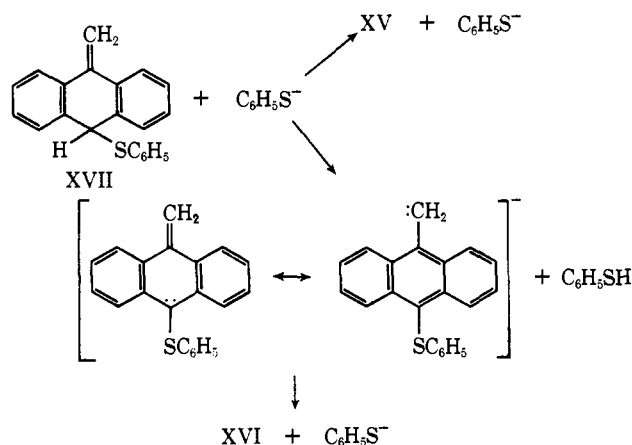
2-nitropropane and benzyltrimethylammonium chloride after 84 hr. These facts are readily intelligible on the basis of the proposed multistage mechanism.

The matter of concertedness or nonconcertedness[6] in the formation, and isomerization, of intermediates such as VI is being studied. Also under investigation are numerous interesting questions relating to leaving groups, nucleophiles, and ring systems.[7]

Acknowledgment. We thank the National Science Foundation and Eli Lilly and Co. for generous support. We are indebted to Dr. P. R. Singh for valuable preliminary studies and to Mr. D. C. Williams who prepared some of our starting materials and checked certain experiments.

(4) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press, New York, N. Y., 1962, pp 55–60.
(5) Prolonged treatment of XV with sodium thiophenoxide does not isomerize it to XVI.
(6) F. G. Bordwell, Accounts Chem. Res., 3, 281 (1970).
(7) The question arises: do we deal here with one-electron transfer processes, i.e., are radicals and radical anions involved? Preliminary studies of the reaction of eq 2 do not support this possibility for the reaction is unaffected by oxygen and by di-tert-butyl nitroxide; the matter is being investigated further.

C. Wayne Jaeger, Nathan Kornblum*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

The Carbatricobalt Decacarbonyl Cation.
A Novel Acylating Agent

Sir:

During a study of C-functional derivatives of methylidynetricobalt nonacarbonyl, we became interested in the chemistry of carboxymethylidynetricobalt nona-

carbonyl (1a). In the course of this work, we have developed the preparation of the novel title compound (as the PF_6^- or BF_4^- salt) and have found it to be a reactive acylating agent with potentially important applications.

Carboalkoxymethylidynetricobalt nonacarbonyls (1, R = alkyl), generally purple to red-purple crystalline
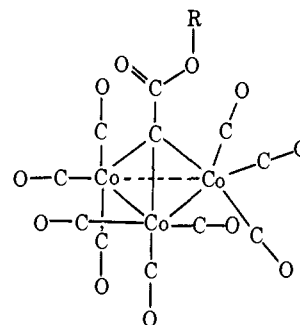
1a, R = H
b, R = Me, mp 108–109°
c, R = Et, mp 45–46°
d, R = Me$_2$CH, mp 63–64°
e, R = Me$_3$C, mp 48–49°
f, R = Me$_3$Si, mp 60–62°
g, R = CH$_2$ = CHCH$_2$, mp 40–41°

solids, can be prepared by reaction of the appropriate esters of trichloroacetic acid with dicobalt octacarbonyl in tetrahydrofuran medium.[1] However, we found that the acid itself cannot be prepared directly by this procedure and that hydrolysis of such esters (1b–1f) to the desired $(OC)_9Co_3CCO_2H$ in THF–water medium using added mineral acids in catalytic or above stoichiometric amounts could not be achieved. As can be seen from the disposition of the carbon monoxide ligands in 1,[2] the ester carbonyl group is in a very sterically hindered environment and this led us to consider as a last resort the reaction conditions which were successful in the hydrolysis of esters of the highly hindered 2,4,6-trialkylbenzoic acids,[3,4] i.e., a reaction in concentrated sulfuric acid.[5] Accordingly, a sample of 1c was dissolved in concentrated sulfuric acid and the resulting yellow-brown solution was poured onto cracked ice. Extraction with ether, followed by evaporation of the dried extracts and crystallization of the residue from chloroform, gave $(OC)_9Co_3CCO_2H$, purple-black needles, which decomposes without melting, $\nu_{C=O}$ 1630 cm^{-1}, in 98% yield. Esterification of this acid by standard procedures using catalytic or above stoichiometric amounts of H_2SO_4 in the presence of the appropriate alcohol as solvent was not successful. However, here the Newman technique[4] also was applicable. When a concentrated sulfuric acid solution

(1) W. H. Dent, L. A. Duncanson, R. G. Guy, W. H. B. Reed, and B. L. Shaw, Proc. Chem. Soc., 169 (1961).
(2) The structure shown for 1 is based upon the results of an X-ray crystal-structure determination for CH$_3$CCo$_3$(CO)$_9$ by P. W. Sutton and L. F. Dahl, J. Amer. Chem. Soc., 89, 261 (1967).
(3) H. P. Treffers and L. P. Hammett, ibid., 59, 1708 (1937).
(4) M. S. Newman, ibid., 63, 2431 (1941).
(5) In general, cobalt carbonyls are not stable to concentrated sulfuric acid. The conversion of acetylenedicobalt hexacarbonyl complexes, (RC$_2$H)Co$_2$(CO)$_6$, to alkylidynetricobalt nonacarbonyls, RCH$_2$·CCo$_3$(CO)$_9$, by treatment of the former with dilute aqueous methanolic H$_2$SO$_4$ has been noted,[6] but nothing was known concerning the effect of concentrated H$_2$SO$_4$ on the RCCo$_3$(CO)$_9$ cluster compounds.
(6) R. Markby, I. Wender, R. A. Friedel, F. A. Cotton, and H. W. Sternberg, J. Amer. Chem. Soc., 80, 6529 (1958).