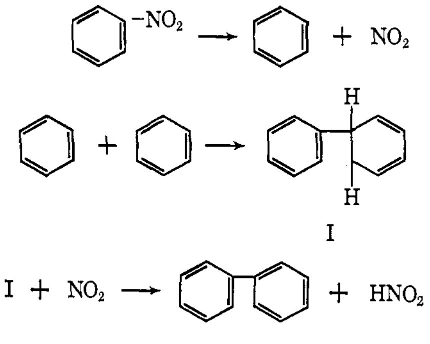
We have discovered a new method for arylating aromatic compounds and heterocyclic compounds of aromatic character. This consists of heating mixtures of nitroaromatics and aromatics at 400–600° in a flow reactor for 2–30 sec. In a typical reaction, a mixture of 5.11 ml (0.05 mole) of nitrobenzene and 22.23 ml (0.25 mole) of benzene was passed through a Vycor tube filled with Vycor chips at 600° under dry nitrogen flowing at 45 cc/min, with a contact time of 9 sec. The vapors were condensed in a bulb at −60°. The condensate was distilled to recover 15.3 ml of benzene and give 8.8 g of product, which consisted of 62% biphenyl and 13.9% terphenyl.[3] Combined yield of biphenyl and terphenyl was 85 mole %. Under identical conditions the same amount of benzene alone gave 0.3 g of product, consisting of 90% biphenyl and 8% terphenyl.

The reaction of nitrobenzene with benzene, run under helium to determine the fate of the nitro group, indicated the course.[4]



$$2HNO_2 \longrightarrow H_2O + N_2O_3$$

The free-radical nature of the reaction was further shown by phenylation of pyridine with nitrobenzene at 600° in 72% yield. Isomer distribution, determined by gas chromatography, was (isomer, %): 2-, 63.6; 3-, 26.3; 4-, 10.1. This distribution is similar to that obtained at 80° by attack of phenyl radicals from the decomposition of benzoyl peroxide on pyridine (isomer, %): 2-, 58; 3-, 26; and 4-, 14.[5]

With thiophene, nitrobenzene (1:5 mole ratio) gave a 60 mole % yield of phenylthiophenes, of which 75% was 2-phenylthiophene and 25% 3-phenylthiophene.[6] Phenylation of thiophene with benzoyl peroxide and three other phenyl radical precursors has likewise led predominantly to 2-phenylthiophene, although the ratios varied over a wide range; the best yield of phenylthiophenes was only 3.75%.[7] The nitrobenzene reaction also gave 3.6 and 0.24%, respectively, of diphenylthiophene and triphenylthiophene or isomers (available data do not differentiate between further phenyl substitution on the phenyl and thienyl rings).

Aromatic compounds containing more than one nitro group can also be used as arylating agents; this greatly increases the versatility of the reaction. Thus, *m*-dinitrobenzene with benzene (1:10 mole ratio) at 450° gave a mixture (40% yield) of 3-nitrobiphenyl and *m*-terphenyl in the ratio 7:1. With increasing temperature at the same contact time (16 sec) this ratio decreased, and at 600° the ratio of the two products was 1:2. At 28-sec contact time and 600° no nitrobiphenyl survived, and *m*-terphenyl was the major product (37%).

Trinitrobenzene behaved similarly in its reaction with benzene at 450–600°. It gave the three products triphenylbenzene, nitroterphenyl, and dinitrobiphenyl in varying ratios that depended upon the temperatures and contact times.

This new reaction appears to be of wide scope and considerable synthetic utility. It has many advantages over present methods of generating free aryl radicals by thermal decomposition of aroyl peroxides[8] or photolysis of aryl iodides;[9] a great variety of nitroaromatics are readily and abundantly available, or easily made. Thus, for example, arylations have been achieved by such diverse nitroaromatics as 1-nitronaphthalene, *m*-nitrobenzotrifluoride, methyl *p*-nitrobenzoate, and 4-nitro-*o*-phenylenediamine. We are presently studying application of our new method in preparing many compounds hitherto unknown or difficult to make by conventional syntheses.

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[3] Small amounts of phenol and naphthalene among the products from the reaction of nitrobenzene with benzene suggest parallels between the thermal processes and those occurring under electron impact. *Cf.* S. Meyerson, I. Puskas, and E. K. Fields, *J. Am. Chem. Soc.*, **88**, 4974 (1966). Such parallel behavior has been demonstrated in other systems: E. K. Fields and S. Meyerson, *Chem. Commun.*, 474 (1965); 275 (1966); *J. Org. Chem.*, **30**, 937 (1965); **31**, 3307 (1966); *J. Am. Chem. Soc.*, **88**, 2836 (1966); R. F. C. Brown and R. K. Solly, *Australian J. Chem.*, **19**, 1045 (1966); M. P. Cava, M. J. Mitchell, D. C. DeJongh, and R. Y. Van Fossen, *Tetrahedron Letters*, 2947 (1966).

[4] For the structure of nitrous acid in the gas phase and its dissociation products, see A. P. Cox and R. L. Kuczowski, *J. Am. Chem. Soc.*, **88**, 5071 (1966), and references cited therein.

[5] D. H. Hey and G. H. Williams, *Discussions Faraday Soc.*, **14**, 216 (1953); R. L. Dannley, E. C. Gregg, Jr., R. E. Phelps, and C. B. Coleman, *J. Am. Chem. Soc.*, **76**, 445 (1954); R. L. Dannley and E. C. Gregg, Jr., *ibid.*, **76**, 2997 (1954).

[6] Authentic 2- and 3-phenylthiophenes for standards in gas chromatographic analysis of the arylation products were synthesized according to J. L. Melles and H. S. Backer, *Rec. Trav. Chim.*, **72**, 325, 491 (1953).

[7] C. E. Griffin and K. R. Martin, *Chem. Commun.*, 154 (1965).

[8] G. H. Williams, "Homolytic Aromatic Substitutions," Pergamon Press, New York, N. Y., 1960, Chapter 3.

[9] W. Wolf and N. Kharasch, *J. Org. Chem.*, **26**, 283 (1961).

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New and Facile Substitution Reactions at Tertiary Carbon

Sir:

Few, if any, authentic SN2 displacements involving tertiary halides are known.[1] Instead, tertiary halides usually undergo substitution *via* the carbonium ion mechanism.

We wish to report a new type of substitution at tertiary carbon which is described by eq 1; a variety of anions are effective.

For example, the reaction of *p*-nitrocumyl chloride (I) with sodium thiophenoxide in DMF solution at 0° is complete in 2 hr and produces the pure tertiary sulfide II (A = SC_6H_5)[2] in 95% yield. That this result does not derive from an elimination reaction

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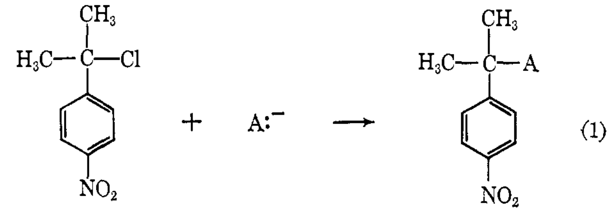
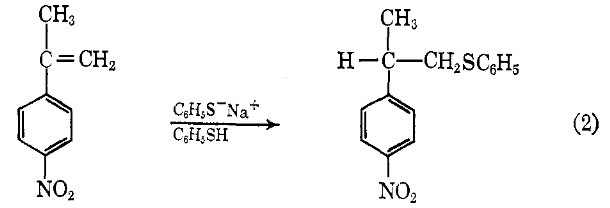
[1] For example, the alleged SN2 Finkelstein substitutions of *t*-butyl bromide have been shown to be spurious by S. Winstein, S. Smith, and D. Darwish, *Tetrahedron Letters*, **16**, 24 (1959). See, however, U. Miotti and A. Fava, *J. Am. Chem. Soc.*, **88**, 4274 (1966).

[2] Satisfactory elemental analyses have been obtained for all new compounds and all structures have been confirmed by nmr.



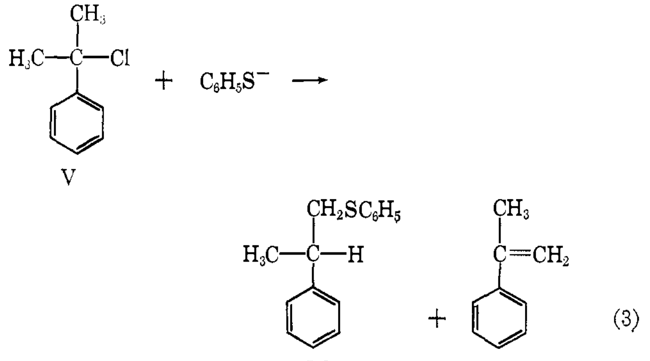
I II

followed by addition of thiophenoxide (or thiophenol) to the olefin III is demonstrated by the fact that the isomeric sulfide IV is produced when olefin III is treated with an equimolar mixture of sodium thiophenoxide and thiophenol (eq 2); furthermore, the reaction of eq 2 is much slower than that of eq 1.



III IV

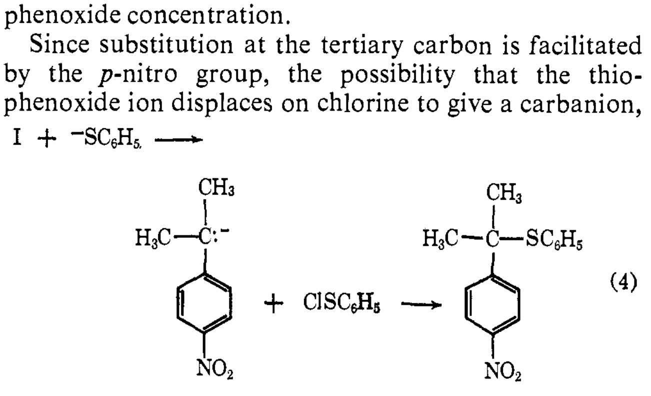
Cumyl chloride (V), in contrast to *p*-nitrocumyl chloride (I), reacts but slowly with sodium thiophenoxide. Not only are 10 days required for complete reaction but a different path is followed. None of the tertiary sulfide, $C_6H_5C(CH_3)_2SC_6H_5$, can be detected; instead the primary sulfide, VI, is obtained in 56% yield[3] along with a 6% yield of VII (eq 3). The fact that cumyl chloride does not undergo substitution at the tertiary carbon atom whereas *p*-nitrocumyl chloride does so readily argues against a carbonium ion mechanism for the reaction of eq 1, a view which is confirmed by the dependence of rate on the sodium thiophenoxide concentration.



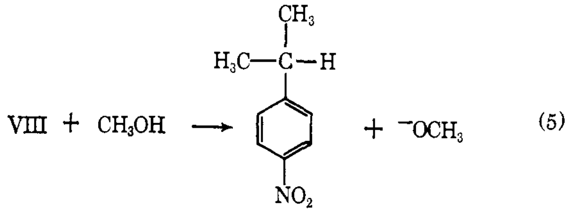
V

VI VII

Since substitution at the tertiary carbon is facilitated by the *p*-nitro group, the possibility that the thiophenoxide ion displaces on chlorine to give a carbanion, VIII, which then gives rise to the observed product (eq 4), must be considered. One would anticipate, if a carbanion is indeed an intermediate, that when the reaction is conducted in DMF containing 20 moles of methanol for each mole of *p*-nitrocumyl chloride a significant fraction of the carbanions would be scavenged by the methanol[4] (eq 5). But, in actuality, methanol does not change the course of the reaction: a 93% yield of the pure tertiary sulfide (II, A = SC_6H_5) is isolated and *p*-nitrocumene (IX) cannot be detected.



VIII



IX

In the same way, the reaction of *p*-nitrocumyl chloride (I) with the lithium salt of 2-nitropropane at 25° in DMF, or in DMSO, follows eq 1 and produces the highly branched carbon alkylate II (A = $C(CH_3)_2NO_2$) in 65% yield. It is noteworthy that covalency formation occurs at the more hindered of the two available positions of this ambident anion despite steric hindrance at the tertiary carbon atom of I. Furthermore, treatment of I with sodium nitrite in DMSO at 25° gives 92–95% yields of the dinitro compound, p-$O_2NC_6H_4$-$C(CH_3)_2NO_2$, a result again illustrative of the insensitivity of these reactions to steric hindrance. Malonic ester anions also react according to eq 1, *e.g.*, II, A = $CH(COOC_2H_5)_2$, is obtained in 84% yield and II, A = $CH_3CH_2CH_2CH_2C(COOC_2H_5)_2$, is isolated in 78% yield. Significantly, monoalkylated malonic ester anions react more rapidly than $\bar{C}H(COOC_2H_5)_2$. Finally, the sodium salt of 1-methyl-2-naphthol reacts with I at 0° in DMF according to eq 1, giving the tertiary ether in 62% yield. Oxygen alkylation is consonant with the facility with which the β-naphthoxide ion undergoes oxygen alkylation in a Michael reaction.[5] In no instance is the reaction of eq 1 observed with cumyl chloride (V).

It seems very likely that these substitution reactions at a tertiary carbon atom are radical anion processes.[6] The insensitivity to steric hindrance becomes intelligible on this basis: reaction is initiated by a one-electron transfer to the unhindered π system of I (eq 6); the resulting radical anion $I\cdot^-$ then goes to the free radical X by losing chloride ion (eq 7); because it is a free radical and is planar (or nearly so), X reacts with the anion, A^-, with ease (eq 8), and, finally, the radical anion XI readily transfers an electron to I (eq 9), thereby producing the product and perpetuating the chain. Steric hindrance has but minimal opportunity to exert itself anywhere in this sequence.

The observation that $CH_3(CH_2)_3\bar{C}(COOC_2H_5)_2$ reacts more rapidly than $H\bar{C}(COOC_2H_5)_2$ is also understandable. Because of its greater degree of alkylation, the monoalkylated malonic ester anion is somewhat less

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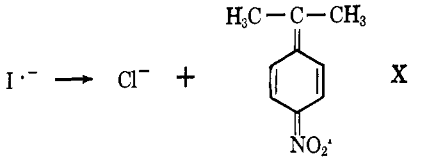
[3] The reaction of olefin VII with an equimolar mixture of sodium thiophenoxide and thiophenol produces the primary sulfide VI.

[4] I. J. Borowitz and R. Virkhaus, *J. Am. Chem. Soc.*, **85**, 2183 (1963).

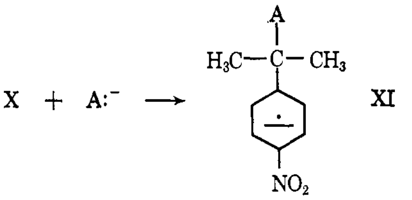
[5] G. B. Bachman and H. Levine, *ibid.*, **69**, 2341 (1947); also see ref 6.

[6] N. Kornblum, R. E. Michel, and R. C. Kerber, *J. Am. Chem. Soc.*, **88**, 5660 (1966); G. A. Russell and W. C. Danen, *ibid.*, **88**, 5663 (1966).

$$I + A\colon^{-} \longrightarrow I\cdot^{-} + A\cdot \qquad (6)$$



X (7)

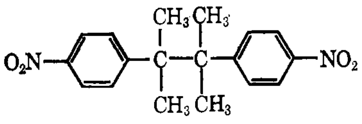


XI (8)

$$XI + I \longrightarrow II + I\cdot^{-} \qquad (9)$$

stable than the anion of malonic ester itself. On the other hand, the free radical A· (eq 6) will be more stable when derived from the monoalkylated malonic ester anion. The two effects reinforce each other and lead to a relatively high reactivity for the monoalkylated malonic ester anion.

Consistent with the proposed radical-anion mechanism is the fact that various of these reactions exhibit some of the following characteristics: light speeds up the reaction, *p*-dinitrobenzene (or oxygen) retards the reaction, the dimer XII is isolated in 1–5% yields.[7]



XII

Aside from their mechanistic significance, the reactions of eq 1 have considerable interest because they provide a facile means of synthesizing highly ramified structures.

Acknowledgment. We thank the Petroleum Research Fund, The Explosives Department of the Du Pont Company, The Purdue Research Foundation, The National Science Foundation, and The Union Carbide Corporation for generous support.

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(7) All reactions were conducted under nitrogen or argon.

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Additions and Corrections

Editor's Note: Hereafter additions and corrections to articles published in the *Journal of the American Chemical Society* will appear in this section promptly after they are received by the Editor. Authors are urged to submit such items when they become aware of the necessity, rather than deferring them to the final issue of the year.

Transition Metal Complexes of Triethylenetetramine. III. *cis*-*α*-**Diacidotriethylenetetraminechromium(III) Complexes** [*J. Am. Chem. Soc.*, **88**, 2156 (1966)]. By D. A. House and Clifford S. Garner. Department of Chemistry, University of California, Los Angeles, California 90024.

In Table I, the value 2950 in column 3 should be 2940, the value 1212 in column 4 should be 1312, and the value 1018 in column 7 should be 1028. On page 2161, in paragraph 2 of column 2, the calculated analysis of 32.9 is for Cl, not C.

Kinetics and Mechanism of the Gas Phase Reaction between Iodine and Isopropyl Alcohol and the Tertiary Carbon–Hydrogen Bond Strength in Isopropyl Alcohol [*J. Am. Chem. Soc.*, **88**, 3480 (1966)]. By R. Walsh and S. W. Benson. Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, California.

The following lines were inadvertently omitted from page 3481. They belong immediately after the last line of text on that page and before the first line of text on page 3482.

"..... ent effect and was finally traced to losses (~1%) of *i*-C_3H_7OH to the grease. Since these could not be avoided, it was not possible to measure precisely the importance of reaction D (also a pressure increase reaction). Analysis showed it to be almost negligible until beyond 50% reaction, and this was confirmed by ......"

Polarographic Study of Coordination Compounds with Delocalized Ground States. Substituent Effects in Bis- and Trisdithiodiketone Complexes of Transition Metals [*J. Am. Chem. Soc.*, **88**, 4876 (1966)]. By D. C. Olson, V. P. Mayweg, and G. N. Schrauzer. Shell Development Company, Emeryville, California, and The Institute of Inorganic Chemistry, The University, Munich, Germany.

The values of m in Table IV should have the opposite sign, $m = 0\ -1,\ -2$. On page 4882, column 2, line 5, $ReS_6C_6Ph_6^{-2}$ should read $ReS_6C_6Ph_6^{-3}$.

The Synthesis of a 4′,5′-Unsaturated Nucleoside [*J. Am. Chem. Soc.*, **88**, 5684 (1966)]. By J. P. H. Verheyden and J. G. Moffatt. Institute of Molecular Biology, Syntex Research, Palo Alto, California.

On page 5685, column 1, line 12, the formula $C_{13}H_{15}N_2O_7$ should read $C_{13}H_{15}N_2O_7I$. On the same page, column 1, line 26, the formula $C_{13}H_{14}N_2O_6$ should read $C_{13}H_{14}N_2O_7$.