(ϵ 3200).[13,14] Addition of HBF_4 led to regeneration of the spectrum of **4**.

When a solution of 0.1 mmol of **5** in 0.4 ml of DMSO-d_6, obtained as described above, was treated with 10 μl of D_2O, H-2,6 and H-4 of **5** were found to undergo exchange for deuterium to the extent of *ca.* 83 and 12%, respectively, in 19 min, and 80 and 25% in 36 min, at *ca.* 35°; no exchange of the S-methyl protons was detectable.[15] The thiinium salt **4** also underwent very slow exchange of H-2,4 and 6 under similar conditions, indicating that an equilibrium between **4**, **5**, and the 4*H* isomer of **4** probably occurs.

Addition of acetic acid-d_4 to a solution of **5** in DMSO-d_6 effected rapid conversion of **5** to **4**-d_4 (δ 3.00 [s, 3] and 7.2–7.8 [m, 10]) with no detectable incorporation of deuterium in the S-methyl group; this result is in contrast to the behavior of **1** in DMSO-d_6 containing increasing amounts of acetic acid-d_4 in which exchange of the S-ring protons occurred to give **1**-d_3, but none of the corresponding 2*H*-thiinium 1-oxide-d_4 could be detected (nmr).

The nmr spectra and deuterium exchange results described above indicate especially high shielding of H-2,6 and pronounced carbanionic character for C-2,6 and C-4 in **5**. Comparison with analogous data for **1** (which are *qualitatively* similar) suggests that ylide-type bonding[4,5] predominates in both **1** *and* **5**. Our nmr results also cast some doubt on the recent claim of a synthesis of 1-phenylthiabenzene,[2] for which *all* the S-ring protons are reported to occur at δ 7.2. The only other known thiabenzene is 1,2,4,6-tetraphenylthiabenzene (**6**).[3]

The lack of evidence for any appreciable ring current effects in **5** (and **1**) lends support to the general type of bonding scheme first suggested for phosphonitrile chlorides by Dewar, and more recently extended by him to include thiabenzene derivatives;[16] thus, in **1** and **5**, two orthogonal and nonconducting hybrid d orbitals on positively charged sulfur might overlap weakly with the ends of the π system of the remaining pentadienyl carbanion.[17–19] Data (uv) in support of similar bonding in 1,1-diphenylphosphabenzene have been reported.[20]

Studies are continuing on related routes to 1-alkyl- and 1-arylthiabenzenes.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support (Grant No. 3032-A1) of this research.

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(13) The thiabenzene decomposed to the extent of ~3% in 1.1 hr under these conditions.

(14) Although thiabenzene **5** is fairly stable at room temperature in the polar media described, all attempts to extract **5** (under N_2) into less polar solvents (diethyl ether, $CHCl_3$, CCl_4), or to generate **5** in diethyl ether, led to rapid decomposition. Nmr spectra of **5** in these less-polar media showed only minor differences in the values cited above for the chemical shifts of the S-ring protons of **5** in DMSO.

(15) Similar behavior was also observed for **1** under these conditions, but exchange occurred at a considerably slower rate (R. L. Harris, unpublished results); *cf.* Y. Kishida and J. Ide, *Chem. Pharm. Bull.* (Tokyo), **15**, 360 (1967).

(16) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, pp 430–436, and references cited.

(17) Nmr data for pentadienyl carbanions have been reported: R. B. Bates, W. H. Deines, D. A. McCombs, and D. E. Potter, *J. Amer. Chem. Soc.*, **91**, 4608 (1969), and references cited.

(18) The observed alternation in negative charge densities in the carbanions studied by Bates, *et al.*,[17] and the fact that protons on β-carbon atoms in vinyl sulfonium salts are strongly deshielded[19] point out that ylidic character cannot necessarily be discounted for 1,2,4,6-tetraphenylthiabenzene (**6**) on the basis of the nmr data reported by Suld and Price (cited in ref 3). Also, the low dipole moment (1.88 D) of **6** might be explained as the resultant arising from a higher localization of negative charge at C-2,6 than at C-4 in the S ring of (ylidic) **6**.

(19) M. C. Caserio, R. E. Pratt, and R. J. Holland, *J. Amer. Chem. Soc.*, **88**, 5747 (1966).

(20) G. Markl, *Angew. Chem. Intern. Ed. Engl.*, **3**, 147 (1964).

(21) National Science Foundation Trainee, 1968–1969.

Alfred G. Hortmann, Ronald L. Harris[21]
Department of Chemistry, Washington University
St. Louis, Missouri 63130

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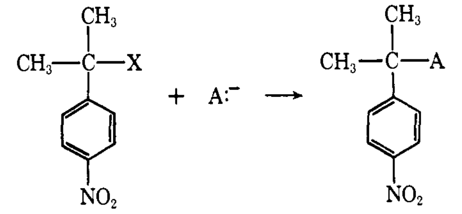
New and Facile Substitution Reactions at Tertiary Carbon. The Reactions of Amines with *p*-Nitrocumyl Chloride and α,*p*-Dinitrocumene

Sir:

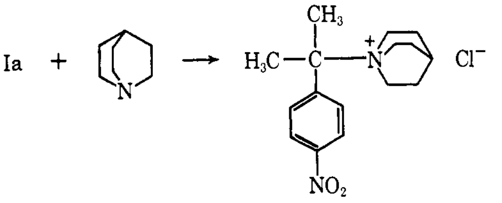
Several years ago we described a new and facile type of substitution at the tertiary carbon atom of *p*-nitrocumyl chloride (Ia) and α,*p*-dinitrocumene (Ib); in these reactions a wide variety of anions smoothly displace the chlorine of Ia, or the aliphatic nitro group of Ib, as shown in eq 1.[1a,b]



(1)

Ia, X = Cl
Ib, X = NO_2

Until now, the nucleophiles employed have always been negatively charged. We now report a set of reactions involving uncharged nucleophiles, namely, amines. Thus, when *p*-nitrocumyl chloride (Ia) is treated with quinuclidine in DMSO at room temperature for 10 hr, a 90% yield of the pure quaternary ammonium chloride (II) is isolated (eq 2). When *p*-nitrocumyl chloride is allowed to react with piperidine, a 91% yield of the pure alkylate is obtained. In the same way various other amines undergo monoalkylation on treatment with *p*-nitrocumyl chloride (Table I). In contrast, although cumyl chloride reacts with quinuclidine (and with piperidine) it gives no alkylate; instead, only α-methylstyrene and cumyl alcohol are produced.



(2)

II

The reactions of Table I might, conceivably, proceed *via* initial elimination followed by Michael addition to the olefin. But from the work of Dale and Buell[2] it is

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(1) (a) N. Kornblum, T. M. Davies, G. W. Earl, N. L. Holy, R. C. Kerber, M. T. Musser, and D. H. Snow, *J. Amer. Chem. Soc.*, **89**, 725 (1967); (b) N. Kornblum, T. M. Davies, G. W. Earl, G. S. Green, N. L. Holy, R. C. Kerber, J. W. Manthey, M. T. Musser, and D. H. Snow, *ibid.*, **89**, 5714 (1967).

(2) W. J. Dale and G. Buell, *J. Org. Chem.*, **21**, 45 (1956).

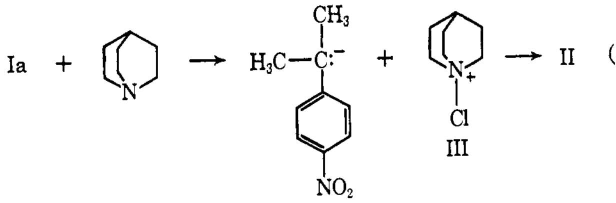
Table I. Reactions of *p*-Nitrocumyl Chloride (Ia) with Amines[a]

Amine	Reaction time, hr	Yield of alkylate, %
Quinuclidine	10	90
DABCO	36	85[b]
Piperidine	18	91
Pyrrolidine	16	90
n-Butylamine	90	67[c]
Di-*n*-butylamine[d]	88[e]	34[c,g]
Methylamine[f]	5	91[c]
Dimethylamine[f]	5	96[c]
Trimethylamine[f]	22	66[g]
Ammonia[f]	428	27

[a] All reactions in DMSO, in the light, under N_2 at *ca.* 35°; [Ia] = 0.2 *M*; unless otherwise stated a onefold excess of amine was used. [b] The product was a mixture of hydrates. [c] By vpc. [d] A fivefold excess of amine was employed. [e] Only 50% reacted; yield not corrected for unreacted Ia. [f] A ninefold excess of amine used. [g] Structure by nmr only.

clear that Michael addition of amines to the olefin produced on removing hydrogen chloride from *p*-nitrocumyl chloride (Ia) would give products isomeric with those actually obtained.

The fact that quinuclidine (and DABCO[3]) react according to eq 2 provides powerful evidence against a carbanion mechanism (eq 3), for, to say the least, the second stage of this sequence, rearward displacement of chloride ion from III by the carbanion, is most improbable.

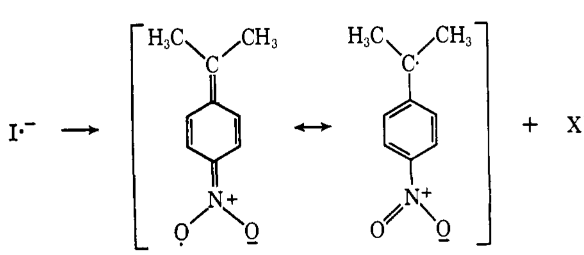


(3)

Substitution of the aliphatic nitro group of α,*p*-dinitrocumene (Ib) also occurs, but the reaction is distinctly less rapid than with *p*-nitrocumyl chloride (Ia). Thus, α,*p*-dinitrocumene (Ib) and piperidine, after 225 hr, give a 77% yield of the monoalkylate.

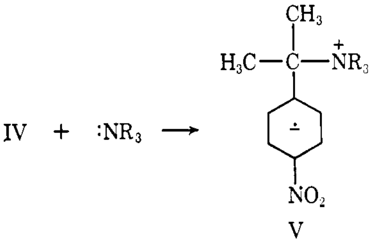
The substitution reactions of eq 1 are believed to proceed *via* a radical anion chain mechanism;[1,4] there is reason to think that the reactions of Ia and Ib with amines follow the analogous sequence (eq 4–7).

$$I + :NR_3 \longrightarrow I\cdot^- + \cdot\overset{+}{N}R_3 \qquad (4)$$



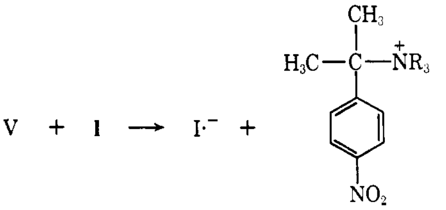
IV

(5)



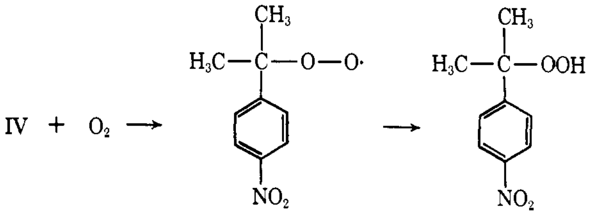
V

(6)



(7)

Oxygen has a profound effect on the reactions of *p*-nitrocumyl chloride with amines. For example, when *p*-nitrocumyl chloride is treated with piperidine under an oxygen atmosphere none of the alkylate is formed; instead, a 55% yield of *p*-nitrocumyl alcohol and a 27% yield of *p*-nitrocumyl hydroperoxide (VII) is obtained. Similarly, oxygen completely suppresses the alkylation of quinuclidine. In the absence of amines oxygen does not affect *p*-nitrocumyl chloride (Ia); the fact that amines induce the conversion of *p*-nitrocumyl chloride to VII and *p*-nitrocumyl alcohol is easily understood on the basis of the proposed mechanism (eq 4–7). Oxygen, an efficient scavenger of carbon free radicals, intercepts the *p*-nitrocumyl radicals (IV) and, thereby, prevents substitution (eq 8); the peroxy radicals (VI) are converted to the hydroperoxide (VII) which, to a greater or lesser extent, is reduced to *p*-nitrocumyl alcohol by the amine,[5a] or by the DMSO employed as solvent.[5b] The isolation of *p*-nitrocumyl hydroperoxide (VII) provides strong support for the view that *p*-nitrocumyl radicals are intermediates in these amine substitution reactions.



VI VII

(8)

When the reaction of *p*-nitrocumyl chloride with quinuclidine is conducted in the usual way, *i.e.*, under nitrogen, it is half over in *ca.* 2.5 hr. But if 1 mol % of oxygen is introduced into the system no reaction can be detected for at least 2 hr; furthermore, when the reaction finally becomes perceptible it proceeds relatively slowly. For 1 mol % of oxygen to produce such a dramatic effect must mean that we deal with a chain process.

Finally, it is noteworthy that the reaction of piperidine with *p*-nitrocumyl chloride proceeds only 30% to completion in 22 hr when the system is maintained in total darkness, but when the system is exposed to an ordinary fluorescent light, the reaction is half over in 2 hr. The alkylation of quinuclidine by *p*-nitrocumyl chloride is also profoundly affected; in the dark it has a half-life of *ca.* 200 hr whereas in the light the half-life is *ca.* 3 hr. Presumably, initiation (eq 4) is speeded up by light; very possibly a charge-transfer complex of I and

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(3) 1,4-Diazabicyclo[2.2.2]octane.

(4) N. Kornblum, G. W. Earl, N. L. Holy, J. W. Manthey, M. T. Musser, D. H. Snow, and R. T. Swiger, *J. Amer. Chem. Soc.*, **90**, 6222 (1968).

(5) (a) G. M. Coppinger and J. D. Swalen, *ibid.*, **83**, 4900 (1961); (b) G. A. Russell and A. G. Bemis, *ibid.*, **88**, 5492 (1966). Also see footnote 5 of ref 4.

amine, on absorbing light, is converted to $I\cdot^-$ and the radical cation of the amine.

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Nathan Kornblum, Francis W. Stuchal
Department of Chemistry, Purdue University
West Lafayette, Indiana 47907
Received November 24, 1969

Detection of Rapid Optical Inversion in "Labile" Cobalt(II) Chelates Using Proton Magnetic Resonance

Sir:

Detailed kinetic and mechanistic studies[1] of optical inversion in tris metal chelates with bidentate ligands generally require the capability of physically separating the isomers. Thus past investigations have been restricted to the "nonlabile" transition metal ions (optical lifetimes $\gtrsim 10^2$ sec). To date virtually nothing is known about the optical lifetimes of chelates of the "labile" metal ions, such as cobalt(II). In particular, it is not even known whether the optical lability is determined by bulk ligand exchange or by some intramolecular process.

Recently[2] it has been shown that for complexes of mixed, symmetric bidentate ligands, $M(CC)_2(DD)$ (CC, DD = dissimilar, symmetric diketonates), the magnetically inequivalent terminal CC methyl groups display slightly different chemical shifts. Optical inversion, which is accompanied by exchange of these methyl groups,[3] was then monitored by observing the collapse of the two methyl signals as the temperature was raised. These observations for mixed β-diketonates of Al(III)[2] and Ga(III)[4] have demonstrated that optical inversion can be studied in complexes with lifetimes as short as $\sim 10^{-2}$ sec. Since only kinetic processes with lifetimes comparable to the chemical shift difference can be obtained from nmr line-width analysis,[5] the limitations to detecting much shorter lifetimes is due to the very small methyl chemical shift differences ($\sim$10 Hz) usually observed in diamagnetic compounds.[4]

We have been able to obtain the lower limit of the rate of optical inversion[3] of (4,7-dimethyl-1,10-phenanthroline)bis(acetylacetonate)cobalt(II),[6] $Co(AA)_2$-(4,7-phen), using proton nmr.[7] Examination of the physical principles which allow the detection of such short lifetimes ($<10^{-6}$ sec) indicates that this method will have some general applicability for cobalt(II) complexes.

The nmr spectrum of a paramagnetic complex differs from that of an analogous diamagnetic compound in that the combination of the contact interaction (arising from delocalized unpaired electrons) and the dipolar interaction (resulting from an anisotropic g-tensor) leads to a sizable, nonlinear expansion of the chemical shift scale.[8] Thus at 300°K, the proton spectrum of this paramagnetic ($S = {}^3/_2$) chelate[6] exhibits six peaks spread over $\sim$80 ppm, where all peaks can be unambiguously identified by relative areas and by phenanthroline methyl substitution. The two AA methyl peaks are equivalent on the nmr time scale at this temperature. As the temperature is lowered, all peaks shift (see Table I), and the AA methyl peak broadens and splits into two equal peaks, each of which progressively decreases in width. The rate of signal collapse is concentration independent and thus first order. Standard analysis[5,9] of the line widths yields $k^{298} \sim 5 \times 10^6$ sec^{-1}, $E_a \sim 13$ kcal/mol, and log $A \sim 16$. The addition of a slight excess of either 4,7-phen, or $(AA)^-$ in the form tetra-n-butylammonium acetylacetonate does not alter either the paramagnetic peak positions or line widths, suggesting that the kinetic process does not directly involve bulk ligand exchange.

Two aspects of our present observations are noteworthy. Firstly, the chemical shift difference between the two AA methyl groups is $\sim$40 ppm at 240°K ($\sim 10^3$ greater than for diamagnetic complexes), and it is this large shift difference which allows us to monitor such a rapid kinetic process. The origin of this magnified magnetic inequivalence of the AA methyl groups can be traced to the expected g-tensor anisotropy[10,11] which characterizes Co(II). Since the symmetry of the complex is only C_2, both axial and rhombic contributions[12] to the dipolar shifts must be considered. Calculations of the axial, $(3 \cos^2 \chi - 1)r^{-3}$, and the rhombic geometric factors, $(\sin^2 \chi \cos 2\Omega)r^{-3}$, for the necessarily *cis* configuration for the complex, which determine the *relative* dipolar shifts,[12] reveal that a basic characteristic of such mixed complexes is that the AA ligands are so disposed relative to the C_2 symmetry axis that, while the geometric factors for the inequivalent AA methyl groups are quite large, they *always* have *opposite signs.* This is true for both the axial and rhombic geometric factors. Thus the dipolar interaction guarantees a large chemical shift difference between the terminal methyl groups. This observation is valid not only for AA^- but can be shown to be a feature of the XX ligand of any $Co(XX)_2(YY)$ complex. We therefore propose that this nmr method will have general applicability in elucidating the kinetics of rapid intramolecular rearrangements, of which optical inversion in $Co(XX)_2(YY)$ type complexes is only one example.

A second point of interest is that, as the data in Table I illustrate, the Curie law[8] is not obeyed, with the 2,9-H shift in fact *decreasing* with decreasing tempera-

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(1) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1966, pp 646–651.

(2) J. J. Fortman and R. E. Sievers, *Inorg. Chem.*, **6**, 2022 (1967).

(3) The analysis in ref 2 has shown that the rate of optical inversion, k_0, and the rate of nmr signal averaging, k_{nmr}, are not necessarily identical but related by the nature of the transition state. Since $k_{nmr} \leq k_0$,[2] the observed k_{nmr} is a lower limit to k_0.

(4) T. J. Pinnavaia, J. M. Sebeson, II, and D. A. Case, *Inorg. Chem.*, **8**, 644 (1969).

(5) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," The McGraw-Hill Book Co., Inc., New York, N. Y., 1959, Chapter 10.

(6) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966).

(7) The complex was prepared in a conventional manner[6] and dissolved in $CDCl_3$. The proton nmr spectra were run on a Varian HR-100 spectrometer.

(8) D. R. Eaton and W. D. Phillips, *Advan. Magnetic Resonance*, **1**, 103 (1965).

(9) Only data in the region of slow exchange were employed in the analysis.

(10) J. P. Jesson, *J. Chem. Phys.*, **47**, 579 (1967).

(11) Thus the analogous magnetically isotropic Ni(II) complex, which is expected to be less labile, exhibits only a single peak for both AA methyl groups between −70 and 55°.

(12) G. N. La Mar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).