Structure of 1,6-Bis(*p*-chlorophenyl)-3,4-diacetyl-1,5-hexazadiene: A Compound with a Highly Electrophilic *N*-Acetyl Group

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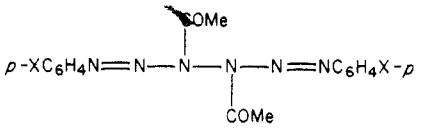
The crystal structure of the title compound (1) shows it to consist of two planar halves, related by C_2 symmetry, in which an extremely long N to acetyl bond (1.403 Å) and a short carbonyl bond (1.200 Å) are the most striking features. These bond lengths, and the unusually high carbonyl stretching frequency (1755, 1742 cm^{-1}), point to strong electrophilic character in the acetyl group of 1. Acetylation by 1 of a variety of aliphatic amines occurs cleanly and with a selectivity which is based on both steric factors and amine basicity. Acetates are formed from alkoxides or phenoxides.

In the meager literature on polyazenes containing more than five contiguous nitrogen atoms reference can be found only to hexazadienes[1,2] and octazatrienes.[3-5] The azo linkages in these require that in principle diastereoisomerism be possible, but there has been no speculation regarding the stereochemistry of any of them.

Though many polyazenes are crystalline solids, and are quite stable, there is no record of any X-ray analysis. We report here the crystal-structure determination of 1,6-bis(*p*-chlorophenyl)-3,4-diacetyl-1,5-hexazadiene (1). It shows some remarkable features which allowed us to predict an otherwise unexpected aspect of its chemistry.



1, X = Cl
2, X = Br
3, X = NO_2

Results and Discussion

The crystal structure and the numbering scheme used in the title compound are shown in Figure 1. All bond angles, except those involving C-H bonds, all bond lengths, and some intramolecular nonbonded distances of interest are shown in Table I.

The molecule in the crystal of 1 has C_2 symmetry, consisting of two planar halves, connected through N(1)–N(1)′ with a dihedral angle of 84.37° (see view along this bond in Figure 1).

The ring to N(3) bond is considerably displaced from the ring bisector. This arrangement evidently minimizes repulsion between the ortho hydrogens and the azo nitrogens since the distances N(3)···H(4) and N(2)···H(8) are approximately equalized.

By far the most remarkable molecular parameter in 1 is the length of the N to acetyl amide bond. At 1.403 (2) Å it is the longest such bond we have been able to find any record of among crystal structures in which the nitrogen is not part of an aromatic system.

Table I. Bond Lengths, Bond Angles, and Some Intramolecular Contacts of Interest in Compound 1

distances, Å		bond angles, deg	
N(1)-N(1)′	1.388 (2)	N(1)′-N(1)-N(2)	119.9 (0)
N(1)-N(2)	1.380 (2)	N(1)′-N(1)-C(1)	118.7 (0)
N(1)-C(1)	1.403 (2)	N(2)-N(1)-C(1)	120.2 (0)
N(2)-N(3)	1.244 (2)	N(1)-N(2)-N(3)	112.7 (0)
N(3)-C(3)	1.429 (2)	N(2)-N(3)-C(3)	113.4 (0)
C(1)-O	1.200 (2)	N(1)-C(1)-O	119.4 (0)
C(1)-C(2)	1.493 (2)	N(1)-C(1)-C(2)	115.6 (0)
C(3)-C(4)	1.390 (2)	O-C(1)-C(2)	125.0 (0)
C(4)-C(5)	1.384 (3)	N(3)-C(3)-C(4)	115.0 (0)
C(5)-C(6)	1.380 (2)	N(3)-C(3)-C(8)	125.2 (0)
C(6)-C(7)	1.380 (2)	C(8)-C(3)-C(4)	119.7 (1)
C(6)-Cl	1.742 (2)	C(3)-C(4)-C(5)	120.6 (1)
C(7)-C(8)	1.383 (2)	C(4)-C(5)-C(6)	118.8 (1)
C(8)-C(3)	1.396 (2)	C(5)-C(6)-C(7)	121.7 (1)
		C(5)-C(6)-Cl	119.7 (0)
C(2)-H(2A)	0.96 (2)	C(7)-C(6)-Cl	118.7 (0)
C(2)-H(2B)	0.93 (2)	C(6)-C(7)-C(8)	119.5 (0)
C(2)-H(2C)	0.94 (2)	C(7)-C(8)-C(3)	119.7 (0)
C(4)-H(4)	0.96 (2)		
C(5)-H(5)	0.94 (2)		
C(7)-H(7)	0.99 (2)		
C(8)-H(8)	0.95 (2)		
N(1)···N(2)′	2.395 (2)		
N(1)···N(3)	2.186 (2)		
N(2)···C(3)	2.237 (2)		
N(2)···N(2)′	3.234 (2)		
N(3)···N(3)′	3.454 (2)		
N(2)···N(8)	2.47 (2)		
N(3)···H(4)	2.45 (2)		

In acetamide itself the value is 1.334 Å[7] and in its *N*-methyl[8] and *N*-phenyl[9] derivatives 1.29_0 and 1.345 Å, respectively. In the only *N*-acetyl polyaza structure we are aware of, 1,2-diacetylhydrazine, the bond length is 1.341 (8) Å.[10] In strainless, nonaromatic cyclic systems, similar C to N bond lengths are observed.[11,12]

The amide C to N bond in 1 is indicative of an unusually low degree of double bond character. Relative to methylamine (C–N, 1.474 Å), the bond shortening is only about

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(2) J. P. Horwitz and W. A. Grakauskas, *J. Am. Chem. Soc.*, **79**, 1249 (1957).

(3) J. C. McGowan and L. Seed, British Patent 834 332 (1960); *Chem. Abstr.*, **54**, 23434e (1960).

(4) A. Wohl and H. Schiff, *Chem. Ber.*, **33**, 2741 (1900); **35**, 1900 (1902).

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(6) The distances between the azo groups in 1 are 3.234 (2) Å between N(2)···N(2)′ and 3.454 (2) Å between N(3)···N(3)′, quite suitable for coordination with metal atoms. However, we failed to obtain any evidence of reaction with aqueous Cu(II), Fe(II), Fe(III), Hg(II), Zn(II), Sn(II), or with $Fe_2(CO)_9$ or $PtCl_2$·cyclooctadiene complex. Both $PdCl_2$·PhCN complex in benzene and $Mo(CO)_6$ in acetonitrile gave intractable products.

(7) W. C. Hamilton, *Acta Crystallogr.*, **18**, 866 (1965).

(8) J. L. Kutz and B. Post, *Acta Crystallogr.*, **13**, 624 (1960).

(9) C. J. Brown, *Acta Crystallogr.*, **21**, 442 (1966).

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(12) P.-E. Werner and O. Rönnquist, *Acta Chem. Scand.*, **24**, 997 (1970).

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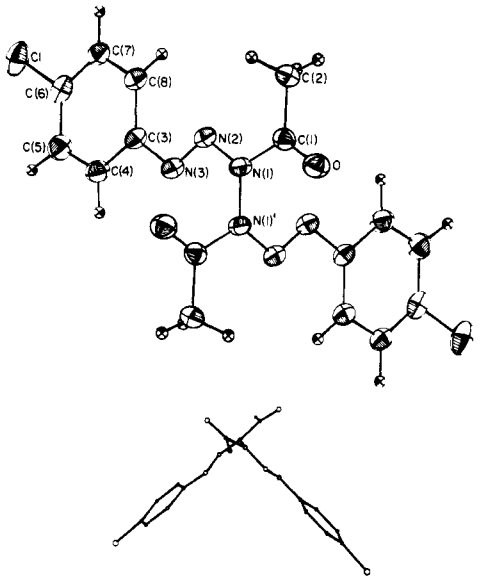


Figure 1. ORTEP plot and side-on view of compound 1.

Table II. IR and ^{1}H NMR Spectral Data of Compounds 1-5

compd	ν (CCl_4) C=O,[a] cm^{-1}	δ ($CDCl_3$) Me	Ar[b]
1	1755, 1742	2.70[c]	7.2-7.6
2	1752, 1737	2.70	7.3-7.7
3	1760, 1746	2.76	7.64, 8.30 (d, J = 9 Hz)
4	1728, 1715	2.50	7.3-7.7
5	1720[d]	2.17, 2.60	7.3-7.6

[a] See ref 21 for comment on multiplicity of peaks. [b] Very closely spaced quartets except in 3. [c] Sharp singlet down to -90 °C. [d] $CHCl_3$.

0.07 Å (similar to the bond shortening in the acyl to O bond in esters compared with the alkyl to O bond in ethers). With such a long C to N bond a shorter than normal carbonyl bond is to be expected. The observed value of 1.200 (2) Å is indeed shorter than in acetamide 1.26 Å,[7] or in any of its derivatives listed above.[8-10]

Bonds comparable in length to the C to N bond in 1 have been recorded only in 1-acetylpyrazole derivatives, both in monocyclic[13] and polycyclic[14] systems. In these, however, the aromaticity of the pyrazole ring can be maintained only with the nitrogen lone pair, and hence, at the complete expense of any delocalization with the CO group, which is thus devoid of normal amide character.[15] In the case of 1 the normal amide resonance may be offset by a contribution from the resonance form **1a**, which allows the observed planarity at amide nitrogen to be reconciled with a long N to C and a short C to O bond.

The values for the formal single and double bonds between nitrogens in 1 are completely in line with those found in 2-tetrazenes,[17,18] and in a variety of triazenes,[19]

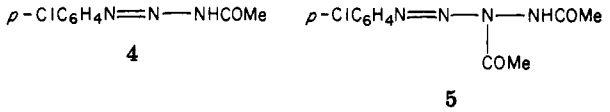
Table III. Half-times of Reaction of 1 with Amines (0.26 M each) in C_6H_6 at 35 °C

entry	amine	half-time, min
1		1.0
2	Me_2NH	6
3	n-$BuNH_2$	13
4		15
5	$PhCH_2NH_2$	64
6	Me_2CHNH_2	100
7	$(n\text{-}Bu)_2NH$	1680
8	Me_3CNH_2	3800
9	$(Me_2CH)_2NH$	$>2 \times 10^5$[a]

[a] No product was observed after 16 days. This value was obtained by assuming a detection limit of 5% and second-order kinetics.

the sole exception being the symmetrical p,p'-bis(bromophenyl)triazene in which the N to N bonds are degenerate.[20]

Predictably the anomalous amide bond lengths of 1 are also reflected in the IR absorptions of the CO group, which occur at 1755 and 1742 cm^{-1} [21] (Table II). The p-bromo and p-nitro analogues of 1, compounds 2 and 3, also gave similar IR spectra. These extraordinarily high values may be characteristic of the N-acyl α-amino azo system. Thus the CO groups in the N-acetyltriazene 4[2] and the N,N'-diacetyltetrazene 5 (which we required in related work) absorb well above 1700 cm^{-1}, although not at as high a frequency as do the hexazadienes[22] (Table II).



4 5

The N-acetyl group in 1 is strongly deshielded in its ^{1}H NMR spectrum, appearing at δ 2.70 (Table II). A significant contribution from resonance structure **1a** is again indicated. Compounds 2 and 3, and the tetrazene 5 in one of its peaks, show the same effect. The methyl peak in 1 remains sharp even down to -90 °C. Either rotation is very fast at -90 °C, or, if it is slow, one rotamer is in very large excess over all others. Given the pronouncedly single-bonded nature of the C to N bond, the former supposition is much more likely.

The amide bond lengths, the high frequency carbonyl absorption, and the deshielding of the methyl group in 1

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(15) Lengthening of a C to N bond over normal values is also caused by the presence of two (imide) or three CO groups on the nitrogen. Here delocalization is "diluted" in each CO group. In tribenzoylamine an additional factor is that the nitrogen is locally nonplanar. The molecule is a shallow pyramid with the benzoyl groups in a staggered, propellor shaped, arrangement (C_3 symmetry). The C to N bond length is 1.440 (2) Å.[16]
(16) P. A. Caron, C. Riche, C. Pascard-Billy, and J.-C. Gramain, *Acta Crystallogr., Sect. B*, **33**, 3786 (1977).
(17) R. Allmann, *Acta Crystallogr.*, **22**, 246 (1967).
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(19) (a) Yu. D. Kondrashev, *Kristallografiya*, **9**, 403 (1964); (b) *ibid.*, **13**, 622 (1968); (c) V. F. Gladkova and Yu. D. Kondrashev, *ibid.*, **13**, 1076 (1968); (d) *ibid.*, **16**, 929 (1971); (e) *ibid.*, **17**, 33 (1972); (f) Yu. D. Kondrashev, *J. Struct. Chem. (Engl. Transl.)*, **15**, 441 (1974).
(20) Yu. D. Kondrashev, *Kristallografiya*, **6**, 515 (1961).
(21) The origin of the doubling of the CO peaks in 1 (or in other compounds discussed here in which it might not be expected) is unclear. It could be due to the presence of a conformation, other than C_2, in solution, the occurrence of amide rotamers (unlikely in view of the above discussion on the amide bond, and on our ^{1}H NMR observations on 1), or to Fermi resonance.
(22) In principle, any effect which reduces the contribution of resonance forms of the type ($^+N{=}C{-}O^-$) will cause a blue shift in the absorption of a CO group attached to nitrogen. An example is found in the acylazo group of azodicarbonyl compounds, in which the polar resonance form $-N{=}{}^+N{=}C{-}O^-$ is forbidden due to the requirement of trigonal geometry at nitrogen. Thus azodiacetyl absorbs at 1767 cm^{-1}.[23] Competing resonance, as discussed for 1, and also as postulated for N-acyl aza heterocycles,[24] are other examples of this effect. Thus competition from aromaticity both raises the IR absorption of the CO group and shortens its bond length while increasing that of the CN bond.

all point compellingly to one chemical expectation, that the acetyl group should be highly electrophilic. Indeed a pointer to this behavior exists in the literature. The acetolysis of 1 occurs very rapidly, in cold 0.3 N ethanolic KOH, to give the triazene 4 and *p*-chlorophenyl azide in high yield.[2] In fact, 1 also reacts in the same way with much milder bases. It shows a high degree of selectivity, at least toward amines, and in this regard it might prove a useful, if somewhat esoteric, acetylating agent.

Reactions were carried out with 1 and equimolar solutions of a variety of amines in benzene (0.26 M) at 35 °C. The half-times for amide formation are shown in Table III and run from 1 min to several days. Both the base strength of the amines (entries 2 vs. 3, 6) and especially steric effects (2 vs. 8, 3 vs. 7, 6 vs. 9) appear to be important. Conformational flexibility in the amine is highly inhibitory, as shown by the reactivity sequence in entries 1, 4, and 7.

In a competitive experiment equimolar amounts of 1, dimethylamine, and isopropylamine reacted to give dimethylacetamide and isopropylacetamide in a ratio of 9:1. Under the same conditions with acetic anhydride in place of 1, the two amides were formed in a ratio of about 2:1.

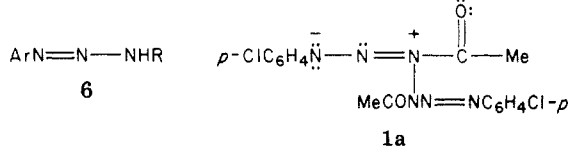
The yields of amide, azide, and 4 are very high. With dimethylamine as base the reaction provides an easy and quantitative preparation of the triazene 4.

The reaction of 1 with aniline was slow and complex; acetanilide and 4 were identified as minor products.

Esterification can be readily achieved. Alcohols themselves are not acetylated, although at reflux other, more complex, reactions occur. Alkoxide and phenoxide anions reacted rapidly in good yields. Thus lithium benzyl oxide and sodium phenoxide gave 73% and 85% of benzyl and phenyl acetates, respectively. Sodium acetate was not acetylated, so anhydride formation is evidently not possible.

In summary, 1 is a more effective acetylating agent than acetate esters but much less so than acetic anhydride or acetyl chloride. The ability to acetylate may be general for α-(*N*-acetylamino) azo compounds. The triazene 4 itself is a case in point, being an exceedingly mild acetylating agent. Thus pyrollidine, the most reactive amine of Table III, reacted cleanly with 4 with a half-time of 9.5 h (570 times longer than with 1). With dimethylamine the half-time was 6 days (1440 times longer than with 1).

Although 4 is a much slower acetylating agent than 1, the related *N*-alkyltriazenes 6 have been found to be rapid alkylating agents.[25] It seems probable, therefore, that 1,6-bis(*p*-chlorophenyl)-3,4-dimethyl-1,5-hexazadiene, a known compound,[26] would be a potent methylating agent.



Experimental Section

The following spectrometers were used: for infrared a Beckman IR 10, for ultraviolet a Unicam SP 800, for NMR a Perkin-Elmer R12 (^{1}H) or a Bruker WP-80 (^{1}H and ^{13}C), for mass spectrometry a Varian VG 7070F. Melting points are uncorrected.

1,6-Diaryl-3,4-diacetyl-1,5-hexazadienes (1–3). These were prepared by the reaction of the appropriate diazonium compound (2 equiv) with 1,2-diacetylhydrazine in aqueous sodium carbonate solution.[2]

***p*-Chloro Compound 1.** Acetone was preferred to benzene as the solvent for purification of the hexazadiene in quantity. Chloroform, in which it is fairly soluble, gave the most suitable crystals for X-ray analysis; these were obtained by slow evaporation: mp 132–134 °C dec (lit.[6] mp 131–133 °C; the melting point is not a good criterion of purity since it depends slightly on the rate of heating); UV (EtOH) λ 2230 (ε 23 700), 2870 Å (27 700); ^{13}C NMR ($CDCl_3$) δ 21.7 (Me), 123.9 (C_2), 129.3 (C_3), 135.9 (C_4), 145.8 (C_1), 168.2 (CO); mass spectrum, *m/e* (based on ^{35}Cl only), no molecular ion, 349 (M − CH_3CO, <1), 139 ($ClC_6H_4N_2^+$, 74), 111 ($ClC_6H_4^+$, 100).

X-ray Analysis of Compound 1. Crystal data: $C_{16}H_{14}Cl_2N_6O_2$; mol wt 393.24; monoclinic; a = 13.863 (1) Å, b = 8.985 (1) Å, c = 14.763 (2) Å, β = 94.37 (1)°; V = 1833.5 (4) Å^3; $F(000)$ = 808; Z = 4, ρ_c = 1.424, ρ_n = 1.42 g cm^{-3}; radiation Mo Kα, λ = 0.710 69 Å; μ(Mo Kα) = 3.81 cm^{-1}; space group $I2/c$ (nonstandard setting of $C2/c$).

Data Collection and Reduction. A crystal (0.42 × 0.40 × 0.31 mm) was mounted on a fully automated Syntex P2, four-circle diffractometer. Accurate unit cell constants were obtained from 15 accurately centered reflections ($20 \leq 2\theta \leq 32°$). Data were collected by the 2θ–θ scan technique out to $2\theta = 60°$. Of a total of 2693 unique reflections measured, 1682 with intensities $I \geq 3\sigma(I)$ were considered observed and used in the structure solution and refinement. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement. Systematic absences hkl, $h + k + l = 2n + 1$ and $h0l$, h and $l = 2n + 1$ were consistent with the space group Ic and $I2/c$. With four molecules to the unit cell, the choice of the latter space group required that the molecule possess either twofold or inversion symmetry. A Wilson plot analysis was consistent with the centrosymmetric space group. All nonhydrogen atoms were determined by direct methods solution (Multan80) with the molecule straddling a twofold axis. The structure was refined by full-matrix least-squares methods. With anisotropic thermal parameters, an R of 0.063 ($R = \sum||F_o| - |F_c||/\sum|F_o|$ was obtained. A difference Fourier at this stage revealed the hydrogen atom positions. The structure was then refined to convergence with R = 0.032 and R_w = 0.035 ($R_w = [\sum(|F_o| - |F_c|)^2/\sum\omega F_o^2]^{1/2}$). An empirical weighting scheme of the form $w^{-1} = 2.38 - 0.049|F_o| + 0.00345|F_o|^2$ was used in the final cycles of refinement. A final difference Fourier indicated maximum residuals of 0.09 e Å^{-3} in the vicinity of the chlorine atom. Atomic scattering factors for all nonhydrogen atoms[27] and scattering factors for hydrogen atoms[28] were obtained from the usual sources. Computer programs used in the structure determination have been listed elsewhere.[29] Interatomic distances and bond angles are given in Table I (see paragraph at the end of paper about supplementary material).

Reaction of 1 with Dimethylamine. Identification of Products. To a solution of 1 (150 mg, 0.124 mmol) in benzene (0.47 mL) in an NMR tube was added a solution of dimethylamine (1.84 M, 69 μL, 0.124 mmol) in benzene. The course of the reaction was monitored in the methyl region by ^{1}H spectroscopy. New peaks for the triazene 4 and *N,N*-dimethylacetamide developed. At completion (ca. 30 min) the spectrum was that of an equimolar mixture of 4 and the amide (in a separate experiment authentic *N,N*-dimethylacetamide was added at the end to confirm the identity of the amide). The solution was evaporated to remove all the benzene, leaving a residue whose IR spectrum (CCl_4) showed all the peaks in a synthetic mixture of 4, *p*-chlorophenyl azide, and the amide. Those of particular diagnostic value were the four bands between 2420 and 2080 cm^{-1} for the azide and the

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(25) (a) E. H. White and H. Scherrer, *Tetrahedron Lett.*, 758 (1961); (b) E. H. White, A. A. Baum, and D. E. Eitel, *Org. Synth.*, **48**, 102 (1968); (c) E. H. White and H. Scherrer, *Tetrahedron Lett.*, 1713 (1969).
(26) V. A. Grakauskas, Doctoral Dissertation, Illinois Institute of Technology, Chicago, IL, 1955.
(27) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, UK, 1969, pp 201–227.
(28) R. F. Stewart, G. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(29) N. J. Taylor, S. E. Jacobson, and A. J. Carty, *Inorg. Chem.*, **14**, 2648 (1975).

CO bands for the triazene at 1728 and 1715 cm^{-1} and the amide at 1658 cm^{-1}.

Synthesis of 1-(*p*-Chlorophenyl)-3-acetyltriazene (4). A solution of 1 (500 mg, 1.25 mmol) in benzene (5 mL) was treated with the above solution of dimethylamine (0.90 mL, 1.63 mmol). After 2 h the almost colorless solution was blown down for 10 h in a stream of nitrogen to a colorless residue (252 mg, 1.25 mmol, 100%) of pure triazene 4. It was recrystallized from ether–hexane and was identical with authentic 4[2] by mixture melting point.

Reaction of 1 with Benzylamine, Isopropylamine, and *tert*-Butylamine. The reaction of 1 and the amine (0.26 M each) in benzene (2 mL) was followed by ^1H NMR spectroscopy in the methyl region and was complete in 3 and 6 days, respectively, for the first two amines but only 75% complete in 25 days in the case of the third. The isopropylacetamide was identified by adding an authentic sample to the NMR tube. Benzylacetamide and *tert*-butylacetamide were isolated by removing the benzene, extracting the residue with cold water (2 × 5 mL) and carefully evaporating the aqueous solutions. The crude amides were crystallized from ether–hexane and identified by mixture melting point.

Relative Rates of Reaction of 1 with Amines. Solutions 0.26 M in both 1 and the amine were made up in benzene as described above and the reactions monitored by ^1H NMR spectroscopy in the aliphatic region. The proportions of products were measured by integration of suitable methyl peaks in 1, the triazene 4, and/or the acetamide. The half-time for amide formation was estimated graphically. The results are shown in Table III. The identity of the product was not confirmed except from those amines whose reactions are described in detail above. In every case, however, a clean reaction was evident from the ^1H NMR spectrum.

Competitive Experiments with Dimethylamine and Isopropylamine. Compound 1. A solution of 1 and the two amines (0.46 M each) in benzene was found to have reacted completely in about 1 h by ^1H NMR spectroscopy. The ratio of dimethylacetamide to isopropylacetamide was 9:1 (integration of *N*-acetyl peaks).

Acetic Anhydride. This experiment was done in the same way, with 1 equiv of acetic anhydride replacing 1. The reaction was instantaneous, the ratio of dimethylacetamide to isoporpylacetamide formed being about 2:1.

Reaction of 1 with Aniline. A solution of 1 (393 mg, 1.0 mmol) and aniline (93 mg, 1.0 mmol) in benzene (5 mL) darkened slowly when refluxed. Insoluble material separated, but peaks due to 4 and acetanilide slowly grew in the ^1H NMR spectrum, their identity being further confirmed by GLC analysis.

Reaction of 1 with Lithium Benzyl Oxide. *n*-Butyllithium (2.2 M in hexane, 0.90 mL, 0.73 mmol) was added to a solution of benzyl alcohol (175 mg, 1.62 mmol) in dry ether (5 mL), followed by powdered 1 (637 mg, 1.62 mmol). The yellow solution formed was neutralized with 88% formic acid. Crystals of the triazene 4, which is rather insoluble in cold ether, separated. Dimethyl phthalate (157 mg, 131 μL, 0.81 mmol) was injected as an internal standard for ^1H NMR analysis, followed by carbon tetrachloride (10 mL) to dissolve the triazene and to permit the ether and hexane to be distilled off by atmospheric pressure fractionation. When the pot volume was reduced to about 2 mL, the column was washed down with $CDCl_3$ (2 mL) and the solution was analyzed. Comparison of the methoxy peak in the dimethyl phthalate with the *N*-methyl peak in the triazene and the acetyl peak in benzyl acetate showed that the yields of the latter two products were 100% and 73%, respectively.

In a separate experiment a solution of the lithium salt (0.30 mmol), prepared as above in dry ether (5 mL), was treated with an excess of 1 (197 mg, 0.50 mmol, thus ensuring complete consumption of the alkoxide). The ether was removed, the residue was extracted with hexane, and the hexane solution was evaporated down to a yellow oil. Distillation under reduced pressure gave an almost colorless liquid shown by comparative IR and NMR spectroscopy to be a mixture of *p*-chlorophenyl azide and benzyl acetate.

Reaction of 1 with Sodium Phenoxide. To a stirred suspension of dry sodium phenoxide (348 mg, 3.0 mmol) in benzene (5 mL) was added 1 (393 mg, 1.0 mmol). A yellow coloration and massive gel formation were rapidly evident. After the mixture was stirred for 12 h the whole was treated with dimethyl phthalate (97 mg, 81 μL, 0.50 mmol), diluted with ether (20 mL), and neutralized with 2 N hydrochloride acid. The organic layer was washed out with water, dried (Na_2SO_4), and fractionated through a short column to a volume of 3 mL. Analysis showed the presence of 4 (93%) and phenyl acetate (84%).

The experiment was repeated on twice the scale but without inclusion of the internal standard or neutralization of the reaction mixture. Filtration, washing of the benzene solution with 2 N sodium hydroxide, drying of the organic phase, and evaporation gave an oil. Distillation under reduced pressure gave a mixture of the azide and phenyl acetate, identified by their IR and ^1H NMR spectrum.

Reaction of 1 with Sodium Acetate. A suspension of sodium acetate (246 mg, 3 mmol) was stirred in benzene (5 mL) containing 1 (393 mg, 1 mmol) at room temperature. There was no reaction even after 10 days, the ^1H NMR spectrum of the benzene solution showing only the methyl singlet of 1.

Acetylations with Triazene 4. A solution of 4 (51 mg, 0.26 mmol) and pyrollidine (18.5 mg, 21.7 μL, 0.26 mmol) in benzene (to a total volume of 1.0 mL, 0.26 M) was kept in an NMR tube at 35 °C. The reaction was half complete after 9.5 h (integration of Me singlet in 4 and in 1-acetylpyrollidine) and complete after 4 days.

A 0.26 M solution of 4 and dimethylamine reacted slowly. After 6 days amide formation was only 50% complete; the product was recognizable as dimethylacetamide by the three methyl singlets in its NMR spectrum.

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Registry No. 1, 10312-71-7; 2, 79991-24-5; 3, 79991-25-6; 4, 79991-26-7; 5, 79991-27-8; 1-acetylpyrrolidine, 4030-18-6; *N,N*-dimethylacetamide, 127-19-5; *n*-butylacetamide, 1119-49-9; 1-acetylpiperidine, 618-42-8; benzylacetamide, 588-46-5; isopropylacetamide, 1118-69-0; *N,N*-dibutylacetamide, 1563-90-2; *tert*-butylacetamide, 762-84-5; pyrrolidine, 123-75-1; dimethylamine, 124-40-3; butylamine, 109-73-9; piperidine, 110-89-4; benzylamine, 100-46-9; isopropylamine, 75-31-0; dibutylamine, 111-92-2; *tert*-butylamine, 75-64-9; diisopropylamine, 108-18-9; *p*-chlorophenyl azide, 3296-05-7; aniline, 62-53-3; acetanilide, 103-84-4; lithium benzyl oxide, 15082-42-5; benzyl acetate, 140-11-4; sodium phenoxide, 139-02-6; phenyl acetate, 122-79-2; sodium acetate, 127-09-3.

Supplementary Material Available: Tables containing equations of the planes in 1, atomic coordinates and thermal parameters for nonhydrogen atoms, and atomic coordinates and isotropic thermal parameters for hydrogen atoms (2 pages). Ordering information is given on any current masthead page.