(bp 30–60°) 19.8 g (82%) of **2b**: mp 119–120°; $[\alpha]^{25}_{\mathrm{D}}$ −77.2° (*c* 1.84, benzene); 97.5% optically pure.

Anal. Calcd for $C_8H_{14}BN$: C, 71.13; H, 10.47; N, 10.39. Found: C, 71.09; H, 10.29; N, 10.35.

(*R*)(+)-α-Phenethylamine–borane (**2a**) was prepared in 78% yield as described above: mp 119–120°; $[\alpha]^{25}_{\mathrm{D}}$ +77.3° (*c* 2.12, benzene).

Reduction of Ketones with 2a and 2b. General Procedure.—To a solution of the ketone (4 mmol) in 20–25 ml of the appropriate solvent was added 4 mmol of **2a** or **2b** (97.5% optically pure), and the resulting solution was stirred for 4 hr at the specified temperature. The solvent was removed *in vacuo*, and the residue was stirred with excess 6 *N* HCl until no further hydrogen evolution (from hydrolysis of unreacted amine–borane) was observed. The aqueous solution was saturated with sodium chloride and extracted with 3 20-ml portions of ether. The combined extracts were washed with 10-ml portions of 3 *N* HCl, 6 *N* NaOH, and brine, and the ether solution was then dried and evaporated *in vacuo*. The colorless residual oil was analyzed by glpc (15% FFAP on Chromosorb W and 15% Carbowax 20M on Chromosorb W). A sample was purified by preparative glpc, and the optical rotation was measured on this purified sample as a solution in ether (α-phenethanol) or 95% ethanol (2-heptanol). Absolute configuration and optical purity were determined from the known values of $[\alpha]^{25}_{\mathrm{D}}$ +54.86° (ether) for (*R*)(+)-α-phenethanol[10] and $[\alpha]^{25}_{\mathrm{D}}$ −11.4° (EtOH) for 2-heptanol.[11]

Reductive Amination of 2-Octanone with 2a or 2b and Ammonia.—A solution of 2-octanone (2.24 g, 17.5 mmol) was dissolved in 50 ml of methanol containing ammonia (3.2 ml of liquid NH_3, 140 mmol) and ammonium bromide (3.43 g, 35 mmol), and either **2a** or **2b** (2.36 g, 17.5 mmol) was added. The resulting solution was stirred at 25° for 48 hr. The methanol was removed *in vacuo*, and the residue was stirred for 10 min with excess 6 *N* HCl. The aqueous solution was washed with two 10-ml portions of ether (2-octanol could be isolated from this ether extract if desired). Solid potassium hydroxide was added to the aqueous layer until the pH of the solution was >12, and the amines were extracted with three 25-ml portions of ether. The combined extracts were dried and evaporated *in vacuo* to give a mixture of α-phenethylamine and 2-octylamine. A sample of 2-octylamine was isolated by preparative glpc (15% FFAP on Chromosorb W) and was converted to its benzamide, mp 78–79.5° (86% yield). Absolute configuration and optical purity were determined by comparison of the rotation of the benzamide with the literature value[12] for (*R*)(−)-2-octylamine benzamide of $[\alpha]^{25}_{\mathrm{D}}$ −28.5° (EtOH).

Reduction Amination of α-Keto Acids with 2a or 2b and Ammonia. General Procedure.—To a solution of 0.9 ml (40 mmol) of liquid ammonia and 0.98 g (10 mmol) of ammonium bromide in 30 ml of methanol was added 5 mmol of α-keto acid or α-keto acid sodium salt. The resulting solution was stirred for 1 hr at 25°. (*S*)(−)-α-Phenethylamine–borane (0.68 g, 5 mmol) was added, and the solution was stirred at 25° for 36–72 hr. Methanol and excess ammonia were removed *in vacuo*, and the residue was brought to pH 1 with 12 *N* HCl. After stirring for 15 min, the acidic solution was made basic with excess ammonium hydroxide and washed with two 15-ml portions of ether (ether wash discarded). The aqueous solution was evaporated *in vacuo*. The residue was dissolved in a minimum volume of distilled water and added to the top of a Dowex 50 column (acid form, 250-mequiv capacity). The column was washed with 1 l. of distilled water, and the amino acid was then eluted with 250 ml of 2 *N* ammonium hydroxide. The ammonium hydroxide solution was evaporated *in vacuo* to give the amino acid as a colorless solid. Tlc analysis on cellulose and silica gel plates (butanol–acetic acid–water, 4:1:1) showed one spot identical with that of an authentic sample (detected by ninhydrin staining). Absolute configuration and optical purity were determined by comparison of the rotation of the amino acids with the published values: (*S*)(+)-alanine, observed $[\alpha]^{25}_{\mathrm{D}}$ +0.32 ± 0.11° (*c* 1.85, 5 *N* HCl), lit.[13] $[\alpha]^{25}_{\mathrm{D}}$ +14.6° (5 *N* HCl); (*R*)(−)-glutamic acid, observed $[\alpha]^{52}_{\mathrm{D}}$ −0.97 ± 0.09° (*c* 3.60, 5 *N* HCl), lit.[14] $[\alpha]^{25}_{\mathrm{D}}$ −31.8° (5 *N* HCl); (*R*)(+)-phenylalanine, observed $[\alpha]^{25}_{\mathrm{D}}$ +1.37 ± 0.25° (*c* 0.81, H_2O), lit.[15] $[\alpha]^{25}_{\mathrm{D}}$ +34.5° (H_2O).

Phenylalanine-^{15}N.—Sodium phenylpyruvate (0.47 g, 2.5 mmol), ammonium nitrate-^{15}N (0.40 g, 5.0 mmol, 95% $^{15}NH_4NO_3$), and **2b** (0.68 g, 5 mmol) were allowed to react for 36 hr and worked up as described above to give 105 mg (25%) of phenylalanine, $[\alpha]^{25}_{\mathrm{D}}$ +1.38 ± 0.35° (*c* 0.87, H_2O). A sample was purified by preparative tlc (silica gel G, 4:1:1 butanol–acetic acid–water) for nitrogen isotope mass spectral analysis, minimum ^{15}N composition 88%.[16]

Registry No.—**2a**, 34566-00-2; **2b**, 34566-01-3; 2-heptanone, 110-43-0; acetophenone, 98-86-2; (*R*)-(+)-α-phenethanol, 1517-69-7; (*S*)(−)-α-phenethanol, 1445-91-6; (*S*)(+)-2-heptanol, 6033-23-4; (*R*)(−)-2-heptanol, 6033-24-5; (*S*)(+)-2-octylamine, 34566-04-6; (*R*)(−)-2-octylamine, 34566-05-7; (*S*)(+)-alanine, 3081-24-1; (*R*)(−)-glutamic acid, 6893-26-1; (*R*)(+)-phenylalanine, 673-06-3; (*R*)(+)-phenylalanine-^{15}N, 673-06-3.

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[10] B. Angelo and G. Vavon, *C. R. Acad. Sci.*, **224**, 1435 (1947).

[11] "Handbook of Chemistry and Physics," 50th ed, 1969, p C-323.

[12] P. A. Levene, A. Ruthen, and M. Kuna, *J. Biol. Chem.*, **120**, 759 (1937).

[13] J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," Vol. 3, Wiley, New York, N. Y., 1961, p 1819.

[14] Reference 13, p 1929.

[15] Reference 13, p 2156.

[16] We thank Adrian Swanson, University of Minnesota Mass Spectrometer Laboratory, for this determination.

Pyrolysis of 2-Acetoxy-2-methylcyclopentane-1,3-dione and 3-Acetoxy-3-methylpentane-2,4-dione

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Pyrolysis of 2-acetoxy-2-alkylcyclohexane-1,3-diones (**1–3**) at ~220° for 3–4 hr affords 60–80% of the related 2-alkylcyclopenten-2-ones (**4–6**), plus acetic acid and carbon monoxide.[1,2] It was of interest to see if this remarkably efficient thermal ring contraction reaction could be extended to other types of 2-acetoxy-2-alkyl-1,3-diones. This paper describes the synthesis and pyrolysis of 2-acetoxy-2-methylcyclopentane-1,3-dione (**7**) and 3-acetoxy-3-methylpentane-2,4-dione (**8**). If an analogous ring contraction were to occur, **7** would yield the as yet unreported 2-methylcyclobutenone (**9**) and provide the prototype of a new synthesis of cyclobutenones. The analogous reaction of **8** would yield methyl isopropenyl ketone (**10**) and perhaps provide a useful method for the synthesis of alkyl vinyl ketones.

The preparation of **7** was accomplished by the reaction of 2-methylcyclopentane-1,3-dione (**11**)[3] with lead tetraacetate, in the same manner as the preparations of **2** and **3**,[2] but the maximum yield of pure **7** was only 3%. Exploration of alternate routes, such as thallium triacetate oxidation[4] of enamines **12** and **13**,[5] or epoxidation of enol acetate **14**,[6] in the hope of ther-

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[1] T. A. Spencer, S. W. Baldwin, and K. K. Schmiegel, *J. Org. Chem.*, **30**, 1294 (1965).

[2] T. A. Spencer, A. L. Hall, and C. F. von Reyn, *ibid.*, **33**, 3369 (1968).

[3] V. J. Grenda, G. W. Lindberg, N. L. Wendler, and S. H. Pines, *ibid.*, **32**, 1236 (1967).

[4] M. E. Kuehne and T. J. Giacobbe, *ibid.*, **33**, 3359 (1968).

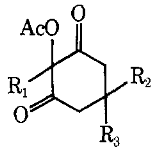
[5] J. J. Panouse and C. Sannié, *Bull. Soc. Chim. Fr.*, 1374 (1956).

[6] B. D. Challand, H. Hikino, G. Kornis, G. Lange, and P. de Mayo, *J. Org. Chem.*, **34**, 794 (1969); D. J. Crispin, A. E. Vanstone, and J. S. Whitehurst, *J. Chem. Soc. C*, **10**, (1970).

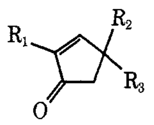
mally rearranging the product to 7,[7] was unpromising; so sufficient 7 for pyrolysis studies was accumulated by the inefficient direct acetoxylation of 11.

Compound 7, mp 62–63°, underwent no change upon being heated at 220° for 1 hr. At 350–400° it reacted to form a distillate of acetic acid (no evidence of 9) and a pot residue of solid black tar. Effluent gases were trapped and shown by vpc analysis to contain less than 7.5% of the carbon monoxide which would be produced by $7 \rightarrow 9$, plus an almost equal amount of methane, which had never been detected in earlier pyrolyses.[1,2]

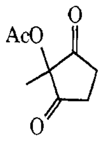
Compound 8, mp 26–27°, was also prepared by lead tetraacetate acetoxylation of the appropriate dione 15 in *ca.* 30% yield. Far from reacting at its boiling point (222°), 8 was essentially completely stable at 320° for 4.5 hr. At 380–400° it reacted to form acetic acid (*ca.* 95%) and a dark residue. No evidence of 10 was obtained, and, again, only a small fraction of the amount of carbon monoxide which would have been produced by the formation of 10 was detected.



1, $R_1 = CH_2CH_2COCH_3$; $R_2 = R_3 = H$
2, $R_1 = CH_3$; $R_2 = R_3 = H$
3, $R_1 = R_2 = R_3 = CH_3$



4, $R_1 = CH_2CH_2COCH_3$; $R_2 = R_3 = H$
5, $R_1 = CH_3$; $R_2 = R_3 = H$
6, $R_1 = R_2 = R_3 = CH_3$



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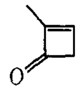

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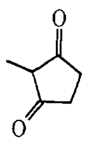

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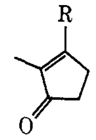
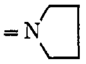
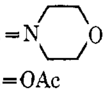
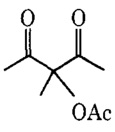


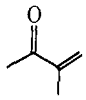
12, R = 

13, R = 

14, R=OAc



8



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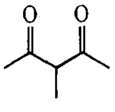

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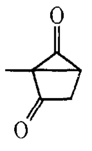

16

The failure of 7 to undergo conversion to 9 is of course explicable on the basis of the ring strain inherent in the product, particularly if the ring contraction proceeds, as is suspected,[2,8] *via* initial 1,3 elimination of acetic acid to form a cyclopropanone, which in the present case would be the very strained bicyclo[2.1.0]dione 16. It is less obvious why the reaction of 8 to form 10 does not occur. 2-Acetoxy-2-alkylcyclohexane-1,3-diones are clearly, perhaps uniquely, predisposed toward such extrusion of carbon monoxide and acetic acid. Even with this class of compounds, the reaction is severely limited as a method of preparing cyclopentenones by the low yields in the acetoxylation step.[9]

Experimental Section[10]

2-Acetoxy-2-methylcyclopentane-1,3-dione (7).—The 2-methylcyclopentane-1,3-dione (11) used in the acetoxylation was prepared by the method of Grenda, Lindberg, Wendler, and Pines,[3] and the lead tetraacetate was prepared, purified, and stored according to the procedure of Fieser.[11] A wide variety of solvents and experimental conditions for the reaction of 9 with lead tetraacetate were tried. Based on previous experience with this type of reaction,[2] we favored conditions, such as those described below, in which only a small amount of the 9 was dissolved, in an attempt to minimize formation of dehydrodimeric products. To a mixture of 30.0 g (0.268 mol) of 9, mp 211–214°, 20 ml of acetic acid, 20 ml of acetic anhydride, and 1000 ml of benzene in a 2-l. flask was added 120 g (0.27 mol) of lead tetraacetate. The flask was covered to keep light out and was stirred overnight. The reaction mixture was filtered to remove 73 g (0.22 mol, 83%) of precipitated lead diacetate. The filtrate was evaporated to a yellow oil to which was added 500 ml of anhydrous ether, producing a yellow, ethereal solution and a yellow, solid residue. The ethereal solution was evaporated and its residue was chromatographed on 700 g of Florisil. Careful elution with 3:7 ether–hexane gave 1.86 g (4%) of crude 7, which was purified by vacuum sublimation to afford 1.30 g (3%) of 7, mp 59–60°. An analytical sample of 7 prepared by recrystallization from ether had mp 62–63°; ir (KBr) 5.75 μ; nmr ($CDCl_3$) δ 1.37 (s, 3, $H_3CC<$), 2.10 (s, 3, H_3CCOO-), and 2.86 ppm (s, 4, $-CH_2CH_2-$).

Anal. Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found: C, 56.40; H, 5.89.

No attempt was made to purify or characterize other products from this reaction, although spectra of crude fractions suggested the presence of dehydrodimeric compounds analogous to those found previously.[2]

Pyrolysis of 7.—Using an apparatus of the type previously described,[1] 4.023 g (0.0236 mol) of 7 in a 10-ml flask was heated at a pot temperature of 220–250° at atmospheric pressure, and with a stream of nitrogen bubbling through it was refluxed through a heating column at *ca.* 370°. A liquid condensed in the apparatus above the heating column which was identified as acetic acid by its ir spectrum. After 35 min, during which time the material in the flask turned black, boiling had essentially ceased. The cooled residue in the flask was 2.027 g of black solid, ir (KBr) 5.90 and 6.2–6.4 μ. Effluent gas, including the nitrogen run through the system, had been collected throughout the pyrolysis. Vpc analysis of this 800 ml of gas on a 5A molecular sieve column[1] showed that it contained less than 5% carbon monoxide (identified by comparison of its retention time with known carbon monoxide prepared by reaction of formic and sulfuric acids), which corresponded to formation of less than a 7.5% yield from 7. The trapped gas also contained a somewhat lesser amount of methane (identified by comparison of its retention time with that of known methane prepared by reaction of methyllithium with water), nitrogen, and oxygen.

3-Acetoxy-3-methylpentane-2,4-dione (8).—3-Methylpentane-2,4-dione (15) was prepared by the methylation of pentane-2,4-dione by the procedure of Johnson, Markham, and Price.[12] Vpc analysis of the product, bp 168–169°, showed that it was a 4:1 mixture of 15 and 3,3-dimethylpentane-2,4-dione, which was used without purification in the acetoxylation. A solution of

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[7] H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, pp 120–121.

[8] R. G. Carlson and J. H. Bateman, *J. Org. Chem.*, **32**, 1608 (1967).

[9] *Cf.* G. Büchi and B. Egger, *J. Org. Chem.*, **36**, 2021 (1971), for a closely related, more effective synthesis of cyclopentenones.

[10] The analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Melting points were taken in an open capillary and are uncorrected. Ir spectra were taken on a Perkin-Elmer Model 137 spectrometer. Nmr spectra were obtained on a Varian Model DA-60-IL instrument. Uv spectra were obtained on a Unicam Model SB 800 spectrometer. Vpc was done on a Wilkens Model A 700 chromatograph.

[11] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1955, pp 325–326.

[12] A. W. Johnson, E. Markham, and R. Price, *Org. Syn.*, **42**, 75 (1962); *cf.* **45**, 68 (1965).

80.3 g of this product, containing *ca.* 62.7 g (0.55 mol) of **15**, in 350 ml of dry benzene was added dropwise over 4 hr to 1 l. of dry benzene, to which was added at the beginning of the reaction and at hourly intervals *ca.* one-fourth of a total of 250 g (0.569 mol) of lead tetraacetate.[11] The reaction was exothermic and maintained itself at *ca.* 35-40°. The yellow reaction mixture was filtered to remove lead diacetate, which was washed with 4 × 100 ml of benzene. The combined benzene layers were washed with 4 × 1 l. of water, dried over sodium sulfate, filtered, and evaporated. The 153.2 g of residue was distilled under reduced pressure to afford benzene (78 g), starting material (4 g), and 58 g, bp 70-165° (3.5-5.5 mm), which was redistilled to afford 17.1 g of starting material, bp 32-45° (1-2 mm), and 29.1 g (31%) of crude **8**, bp 85-145° (1.5-2.5 mm). When placed in the freezer with a small amount of ether, this product solidified to afford, after recrystallization from ether in the cold, 13.4 g (14%) of pure **8**: mp 26-27°; bp 222°; uv max (cyclohexane) 299 mμ (ϵ 84); ir (film) 5.70 and 5.80 μ; nmr (CDCl$_3$) δ 1.67 (s, 3, H_3C-C<), 2.12 (s, 3, H_3CCOO-), and 2.18 ppm (s, 6, 2 H_3CCO-).

Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.69; H, 6.90.

Pyrolysis of 8.—Using an apparatus of the type previously described,[1] 9.74 g (0.056 mol) of **8** in a 25-ml flask was refluxed at a pot temperature of 240° through a heating column at 380-400° for 7 hr. There was obtained 3.94 g of yellow distillate and a dark, solid pot residue. The distillate was found by vpc analysis to be *ca.* 75% acetic acid (*ca.* 95% yield), *ca.* 10% **8**, and *ca.* 15% of an unidentified substance which was not **10**. Ultraviolet spectra of all product fractions indicated that **10** was not present in significant amounts. Effluent gas, including the nitrogen run through the system, was collected during much of the pyrolysis. Vpc analysis of this gas indicated that a maximum of 25% of the theoretical amount of carbon monoxide required for formation of **10** could have been produced.

Registry No.—**7**, 34564-51-7; **8**, 34564-52-8; **9**, 34564-53-9; **15**, 815-57-6.

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A Rational Synthesis of 2-Aminoindazole

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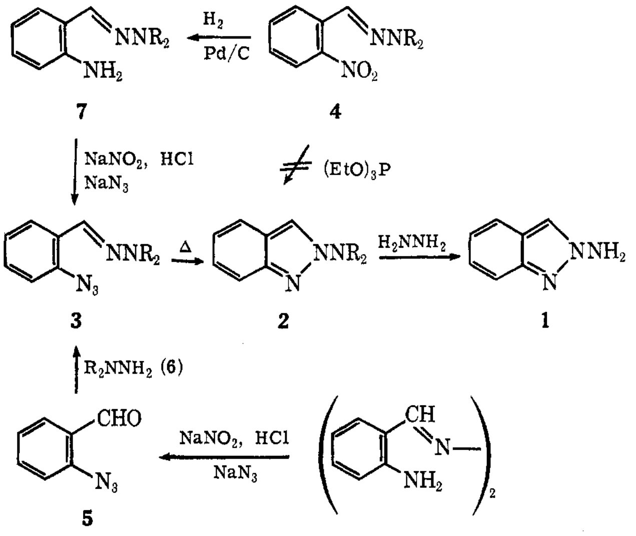
Received December 29, 1971

As a part of our investigation of the chemistry of *N*-nitrenes,[2] it was of interest to study the oxidation of 2-aminoindazole (**1**). This report of the rational synthesis of **1** and of its oxidation is prompted by the recent disclosure of the preparation of both 1- and 2-aminoindazole by the amination of indazole with hydroxylamine-*O*-sulfonic acid.[3]

The scheme used for the preparation of **1** is based on the cyclization of an *o*-nitreno benzaldimine derivative.[4a,b] The failure of our initial attempts to deoxygenate *N*-(*o*-nitrobenzal)aminophthalimide (**4**) to **2**[4] led us to generate the nitrene from the corresponding azide. In this fashion, **1** was obtained in 94% yield from **3** as yellow crystals, mp 96-97°, as illustrated in Scheme I.

SCHEME I



R$_2$ = *o*-phthaloyl

Although **3** was also prepared by the diazotization and azidation of **7**, it was best obtained by the condensation of *o*-azidobenzaldehyde (**5**) with *N*-aminophthalimide (**6**). *o*-Azidobenzaldehyde was synthesized in one step by the diazotization and azidation of *o*-aminobenzaldazine.

Since Rees and his group[3,5] have extensively investigated the oxidation of **1**, we will only briefly describe our results carried out under different experimental conditions. Besides trace amounts of indazole (**12**), 2,2′-biindazole (**13**) was the main product obtained from the oxidation of **1** with mercuric oxide in refluxing *n*-butyl alcohol for 96 hr; in addition, an unstable crude compound exhibiting absorption in the triple bond region was also isolated as a very minor component which may perhaps be the product of the fragmentation of the *N*-nitrene. Addition of a catalytic amount of sodium methoxide gave essentially the same results, although only 2 hr were required in this case. In benzene at room temperature, oxidation with lead tetraacetate gave **12**.

Our results, in conjunction with those of Rees and his students,[3,5] indicate that, under those conditions, fragmentation of 2-indazolyl nitrene (**8**) is not favored, occurring at best only to a minor extent. In view of the difference between Rees' results[2] and ours, it seems likely that the formation of the tetrazane **10**[6] and of the tetrazene **11** does not proceed *via* the *N*-nitrene **8**. Scheme II outlines possible routes which may help explain the products obtained by us. Evidently, the conditions of our oxidations would preclude any possibility of isolation of the 1,2,3-benzotriazine isolated by Rees only in the strict absence of nucleophiles.[3]

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[1] Fellow of the A. P. Sloan Foundation.

[2] K. Sakai and J.-P. Anselme, *Tetrahedron Lett.*, 3851 (1970); K. Sakai, A. Tanaka, G. Koga, and J.-P. Anselme, *J. Chem. Soc. Jap., Pure Chem. Sect.*, **92**, 1065 (1971).

[3] D. J. C. James, S. Bradbury, D. C. Horwell, M. Keating, C. W. Rees, and R. C. Storr, *Chem. Commun.*, 828 (1971).

[4] (a) L. Krbechek and H. Takimoto, *J. Org. Chem.*, **29**, 1150 (1964); (b) P. A. S. Smith in "Nitrenes," W. Lwowski, Ed., Wiley, New York, N. Y., 1970, p 139; (c) J. I. G. Cadogan and R. J. G. Searle, *Chem. Ind.* (*London*), 1282 (1963).

[5] Private communication from C. W. Rees.

[6] D. J. Anderson, T. L. Gilchrist, and C. W. Rees, *Chem. Commun.*, 800 (1971).