τ 8.02, 8.43, 8.38 (sh), and 8.72. The peaks overlapped too much to obtain accurate integrations.

Irradiation of 9 in Ether.—A solution of 9 (448.9 mg, 1.78 mmol) in 350 ml of anhydrous ether was irradiated. The photolysis was followed by the appearance of a maximum at 332 mμ, which reached maximum intensity in 2 hr. The ether was evaporated and the residue was dissolved in methanol and concentrated to a volume of 5 ml. On cooling, crystals (347 mg, 77%) of spiro[1,2,3,4,5,6,7,8,9,10-decahydrophenanthren-10-one-9,1′-cyclopentane] (5) separated, mp 69–70°. The compound was identical (ir, nmr) with material obtained from the low temperature oxidation of 3. No other photoproduct was detected (tlc).

Irradiation of 4 in Ether.—A solution of 4 (770.7 mg, 3.00 mmol) in 400 ml of anhydrous ether was irradiated, the reaction being followed by the decay of a maximum at 253 mμ and the appearance of a new band at 332 mμ. After 4.9 hr the latter band reached maximum intensity, and the reaction was terminated. The ether was evaporated, and the residue, taken up in 15 ml of methanol, showed no unreacted 4 and only one product (tlc). The solution was concentrated to 5 ml, cooled, and afforded 438.4 mg (57%) of dienone 5, identical (melting point, ir, nmr) with an authentic sample. During the photolysis, maxima attributable to 9 appeared, then decayed.

Irradiation of 5.—A solution of 5 (107 mg, 0.42 mmol) in 300 ml of ether was irradiated through a Pyrex filter with a 200-W Hanovia Type S mercury lamp. The photolysis, followed by the disappearance of the band at 332 mμ, was complete in 6.2 hr. Evaporation of the solvent gave an oil different (ir, uv, tlc) from 9. The oil, which had characteristic ir bands at 3500, 1720, 1705, and 1452 cm^{-1} and λ_{max}^{MeOH} 205 mμ (ε 12,300) in the uv, was an acid which was not further characterized.

Dark Reactions.—A solution of dienone 4 (14 mg) in either 5 ml of methanol or 3 ml of ether was stored in the dark for 27 and 36 days, respectively. Analysis by tlc showed that no reaction had occurred, and evaporation of the solvent afforded quantitative recovery of the starting material. Similarly, a solution of 9 (15 mg) in 3 ml of ether kept in the dark for 15 days gave a quantitative recovery of unchanged starting material.

Registry No.—**3**, 1610-39-5; **4**, 17790-43-1; **5**, 17790-44-2; **9**, 17790-45-3; peroxytrifluoroacetic acid-boron fluoride, 17790-46-4.

Acknowledgment.—We are indebted to the National Science Foundation for financial support.

Nitrogen Photochemistry. *syn* and *anti* Isomers of Semicarbazones[1-4]

Virgil I. Stenberg,[5] Paul A. Barks, Dennis Bays, Dwight D. Hammargren,
and Durvasula V. Rao

Department of Chemistry, The University of North Dakota, Grand Forks, North Dakota 58201

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The *syn* and *anti* sets of isomers of several different phenyl ketone semicarbazones have been isolated, and the structural formulas have been assigned. Evidence is presented which demonstrates that the phenyl ring is restricted from rotation in the *syn*-phenyl isomers of the semicarbazones as shown by a diminished amount of conjugation of the phenyl group with the imine double bond. The *syn*-phenyl isomers also have a decreased thermal stability, and, with these isomers, the nmr data clearly portrays that one of the hydrogens of the ureido group is strongly shielded by the phenyl ring confirming the structural assignments.

Although the existence of *syn* and *anti* isomers of semicarbazones has been recognized for some time, there are few cases where both isomers of a semicarbazone have been isolated. In these instances, the structural assignments given are open to question. However, from these earlier experiments certain facts have been learned. The early works of Heilbron and Wilson[6] and of Wilson and Macaulay[7] have clearly demonstrated that *syn* and *anti* isomers of semicarbazones exist and can be interconverted by the agency of ultraviolet light.

Another significant contribution to the history of semicarbazones is the work of Ramart-Lucas and Bruzau.[8] Semicarbazones of phenyl ketones were categorized into two types by means of their uv spectra characteristics, *i.e.*, the "forme absorbante" and the "forme transparente." The phenyl ketone semicarbazones studied had uv spectra which nearly superimposed on one of two general type absorption curves (curves a and b, Figure 1). The "forme absorbante" refers to those semicarbazones which absorb at longer wavelengths. Acetophenone, *p*-methylacetophenone, *p*-methoxyacetophenone, and deoxybenzion semicarbazones have uv spectra approximating that of curve a; and α,α-dimethyldeoxybenzoin, β-phenyl-*p*-methylpropiophenone, and β-phenyl-*p*-methoxypropiophenone semicarbazones have spectra similar to that of curve b. The semicarbazone of α-methyldeoxybenzoin is composed of two isomeric forms which were separated by fractional crystallization from the reaction solution. One of the isomers has an uv absorption spectrum similar to that of curve a in Figure 1, and the other to curve b. A conjugated phenylimine structure of the semicarbazone was postulated for the compounds absorbing with longer wavelengths, and either of two nonconjugated cyclic structures were proposed for the other.

A third important contribution to the background of semicarbazones is the nmr studies of Karabatsos, Graham, and Vane.[9] The nmr spectra were obtained from solutions made by dissolving the crystalline isomer mixtures in trifluoroacetic acid. No separation of the isomers was attempted. The relative chemical shielding of the protons on positions adjacent to the semicarbazone substituent (H_α on I) was measured. The necessary assumption was made that the H_α protons *syn* to the ureido group are more shielded than those *anti* to it. The mixtures of isomeric semicarba-

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(1) Presented before the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstract No. S181.

(2) Taken in part from the Ph.D. Dissertation of D. V. Rao, University of North Dakota, 1965.

(3) Taken in part from the senior thesis of D. D. Hammargren, University of North Dakota, 1967.

(4) This investigation was supported in part by a Public Health Service Research Grant GM 01012-13 from the National Institute of General Medical Sciences, U. S. Public Health Service.

(5) Author to whom requests for reprints should be addressed

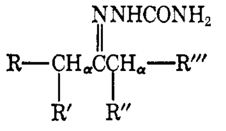
(6) I. M. Heilbron and F. J. Wilson, *J. Chem. Soc.*, **101**, 1482; *Chem. Abstr.*, **7**, 331 (1913).

(7) F. J. Wilson and R. M. Macaulay, *J. Chem. Soc.*, **125**, 841 (1924).

(8) M. Ramart-Lucas and M. Bruzau, *Bull. Soc. Chim. Fr.*, **1**, 119 (1934).

(9) G. J. Karabatsos, J. D. Graham, and F. M. Vane, *J. Amer. Chem. Soc.*, **84**, 753 (1962).

zones all exhibited two absorption bands for the H_α protons, and the relative concentrations of the isomers present in solution could be determined by measuring relative absorption peak areas.



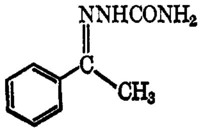
$$\mathrm{R{-}\underset{R'}{\underset{|}{C}}H_\alpha\overset{NNHCONH_2}{\overset{\|}{C}}\underset{R''}{\underset{|}{C}}H_\alpha{-}R'''}$$

I

Thus, it was evident, on tracing the background of semicarbazone chemistry, that there was a need for the actual isolation of the semicarbazone isomers, and the correlation of the uv spectra studies with the later nmr work. Then more positive statements could be made about the structure of the semicarbazones.

The only structure which is in common to the nmr work of Karabatsos, *et al.*,[9] and the uv spectral work of Ramart-Lucas and Bruzau[8] is acetophenone semicarbazone. Potentially it was a structure which could give the proper answer to the cause of the two types of uv spectra of the phenyl ketone semicarbazones and augment the nmr structural assignments.

The melting point of the crystals (II) which result in the preparation of the semicarbazone from the acetophenone and semicarbazide hydrochloride is sharp. These give evidence of being homogenous on analysis with thin layer chromatography. The nmr study of Karabatsos, *et al.*,[9] assigned the concentration of the minor isomer at 10% in a trifluoroacetic acid solution of the crystals. However, since the nmr spectrum was obtained in an acid solution, the major isomer might have equilibrated. As a consequence, isolation of the minor isomer from II was not promising and not attempted.



II

Hence it was desirable to enrich the acetophenone semicarbazone crystals with the second isomer before attempting the isolation. The uv spectrum of II showed that these were of the longer wavelength absorbing type, *i.e.*, "forme absorbante," in confirmation of the work of Ramart-Lucas and Bruzau[8] (curve a, Figure 1). The second isomer was presumed to be the "forme transparente" or of the shorter wavelength absorbing type (curve b, Figure 1). This is the ideal situation in which the optical pumping principle operates, and irradiation with uv light of the appropriate wavelengths was expected to produce an increased concentration of the second isomer.

Since the irradiation was to be done in liquid solution, the limited solubility of acetophenone semicarbazone in organic solvents was one of the principal problems. Although it was soluble in 95% ethanol, irradiation of this solution produced the undesirable product III, and, as a consequence, ethanol could not be used as a solvent.[10] Anhydrous tetrahydrofuran was chosen as an alternate because it was one of the better solvents for the semicarbazone though admittedly poor. Because the phenyl ketone semicarbazones have only one principal uv absorption band (Figure 1) and the medium-pressure mercury arc lamps have a diminished amount of light emmision close to 2000 Å where both isomers absorb equally well, the optical pumping irradiations were done without filters.

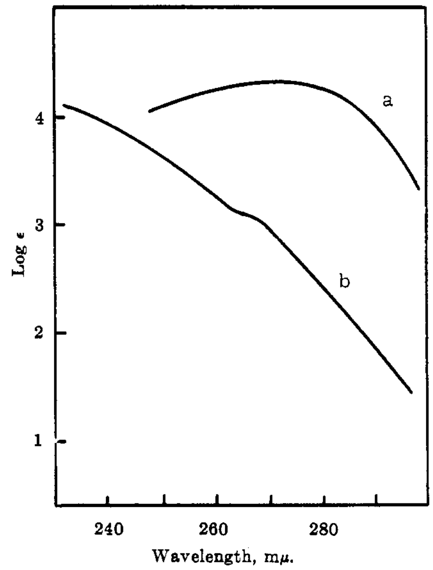
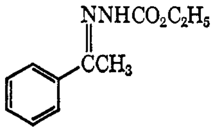


Figure 1.—General shapes of ultraviolet absorption spectra of the two types of phenyl ketone semicarbazones found by Ramart-Lucas and Bruzau.[8] Curve a is the "forme absorbante" and curve b is the "forme transparente."



III

The acetophenone semicarbazone irradiation solution gave a white crystalline compound (IV) in high yield. This photoproduct gave the correct carbon, hydrogen, and nitrogen analysis for an acetophenone semicarbazone and had the proper molecular weight. The photoproduct readily hydrolyzed to acetophenone with aqueous HCl, and it was converted into the 2,4-dinitrophenylhydrazone of acetophenone by the 2,4-dinitrophenylhydrazine reagent solution. The photoproduct isomerized to the starting semicarbazone at its melting point and upon exposure to anhydrous hydrogen chloride when dissolved in an ether solution. It was more soluble in organic solvents than II. From these data, it was obvious that the photoproduct was chemically not very far removed from the starting material, and that it most probably was the desired isomer of the starting material.

The uv spectrum of IV is exhibited in Figure 2. The photoproduct clearly has a more transparent uv spectrum than the starting material II, and, as expected, the spectrum conformed to the second of the two types (curve b, Figure 1) of uv spectra observed by Ramart-Lucas and Bruzau.[8]

The interpretation of the uv spectra was instrumental in the assignment of the appropriate stereo-

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[10] This product can be formed in the solution by heat in the absence of light.

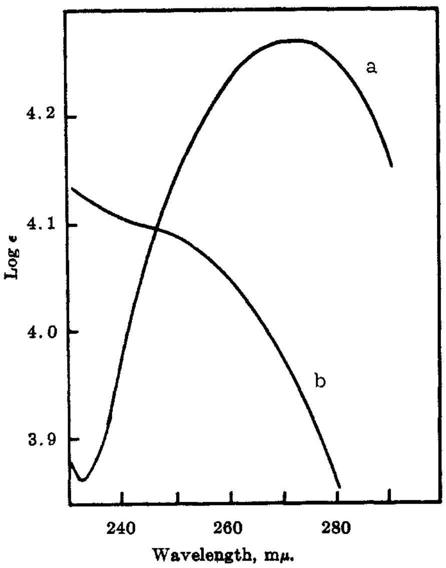
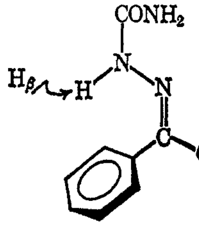


Figure 2.—The ultraviolet spectra of (a) the starting material and (b) the photoproduct of acetophenone semicarbazone.

chemistry to the two isomers. The difference in the absorption between the two isomers is essentially that of the same magnitude difference between the uv maxima of styrene and benzene. This implies that, in the shorter wavelength absorbing isomer IV, the imine bond is not conjugated with the aromatic ring. The uv spectrum of IV can be explained on the basis of steric hindrance. In a study of molecular models, a restricted rotation of the phenyl group in the *syn*-phenyl acetophenone semicarbazone model (IV) was apparent. The π orbital of the imine bond is nearly perpendicular to the π orbitals of the phenyl ring in the model. This is expected to result in a diminished amount of resonance interaction of the two π-bonded systems, and the molecule should have a uv maximum at a shorter wavelength than the *anti*-phenyl isomer. This is true of the photoproduct; as a consequence, its structure is most probably *syn*-phenyl acetophenone semicarbazone.



IV

syn-Phenyl acetophenone semicarbazone IV should be less stable thermodynamically than the *anti*-phenyl semicarbazone because of steric strain. The equilibration with anhydrous HCl in an ether solution provides the more stable II. This, together with the conversion of the photoproduct IV into starting material II at its melting point, clearly portrays the photoproduct as the least stable of the two isomers. This correlates nicely with the predicted lesser stability of the *syn*-phenyl isomer and supplements the structural assignments based on uv spectral data.

By further observing molecular models of the *syn*-phenyl isomer of acetophenone semicarbazone IV, it was obvious that the ureido group position is such that the NH hydrogen of the NNHCO group (H$_\beta$) should be directly over the aromatic ring and immersed in or near the π electrons of the ring. This is a condition in which the proton is expected to be heavily shielded. The same proton in the *anti*-phenyl form does not have such shielding (see structure II). This was expected to influence position of the H$_\beta$ band on the nmr spectra of the two isomers.

The expectations in regard to the nmr spectra did indeed materialize. The H$_\beta$ proton of the starting semicarbazone II occurs at δ 9.38 and the H$_\beta$ of the *syn*-phenyl semicarbazone is δ 7.82, at a difference of 1.56 units. Thus the nmr data further supplements the stereochemical assignments made on the basis of the uv spectral and stability data.

The only remaining feature of acetophenone semicarbazone chemistry to be discussed is the stereochemical assignments made by Karabatsos, *et al.*[9] In trifluoroacetic acid solution it was stated that the *syn*-phenyl isomer IV was present to the extent of 90% and the *anti*-phenyl form at 10%. The hydrogen-bonded structure V was suggested to account for the unexpected results. This assignment was made on the basis that the H$_\alpha$ hydrogens *syn* to the ureido group are *always* more shielded than the H$_\alpha$ hydrogens which are *anti* to it. This assignment we now believe to be open to question.

In tetrahydrofuran, the H$_\alpha$ hydrogens of *anti*-phenyl acetophenone semicarbazone II are shielded slightly more than the *syn*-phenyl form IV. This unexpected result can be attributed to the shielding effect of the phenyl ring on the H$_\alpha$ hydrogens in the *syn*-phenyl isomer. The ring is held in a fairly rigid position, and the H$_\alpha$ protons are affected by the shielding zone of the phenyl ring. This shielding by the aromatic ring is somewhat more pronounced than that of the ureido group. This is most probably true in trifluoroacetic acid solutions also. To check this, *anti*-phenyl acetophenone semicarbazone was dissolved in trifluoroacetic acid, and the sample was allowed ample time to equilibrate. The mixture was quenched by pouring it into water, and the precipitated solid consisted of the *anti*-phenyl isomer of acetophenone semicarbazone as the predominant product. This is a strong indication that the major isomer present in trifluoroacetic acid is the *anti*-phenyl isomer and not the *syn*-phenyl form as previously assigned.[9]

Table I summarizes the nmr data for other semicarbazone isomers isolated in our laboratories. The H$_\beta$ protons exhibited a chemical shift in the order of $1^1/_2$ δ units. In every case the compounds which now could be assigned the *syn*-phenyl form on the basis of the uv spectra have the most shielded H$_\beta$ proton. Since benzophenone semicarbazone must have the *syn*-phenyl form by virtue of its structure, it acts as a standard for the shielded H$_\beta$ proton. The position of its resonance absorption is in the same vicinity as the other *syn*-phenyl isomers.

Although the two benzaldehyde semicarbazones provide the expected relative chemical shifts of the H$_\beta$ protons in the nmr spectra, the absolute values are at a lower field than expected. The *anti*-phenyl isomer proton resonance frequency is at lower field possibly because of the relative shielding ability of the hydrogen in comparison with other substituents attached opposite on the imine group.

TABLE I

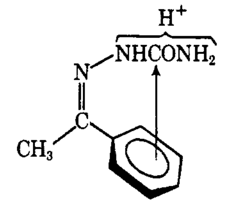
SEMICARBAZONE NMR BANDS

	Semicarbazone	Hβ (δ)	Hα (δ)
1	Benzaldehyde (*syn*-phenyl)	9.09[a,c]	
2	(*anti*-phenyl)	10.33[a,c]	
3	Acetophenone (*syn*-phenyl)	7.82[b,c]	2.20[b,c]
4	(*anti*-phenyl)	9.38[b,c]	2.21[b,c]
5	α-Methyldeoxybenzoin (*syn*-phenyl)	7.67[a,d]	4.02[b,d]
6	(*anti*-phenyl)	9.50[a,d]	4.83[b,c]
7	Deoxybenzoin (*anti*-phenyl)	9.85[a,c]	4.29[b,c]
8	Benzophenone	7.87[b,c]	

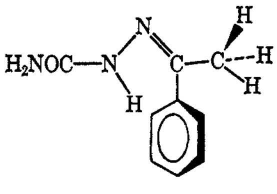
[a] Recorded in DMSO. [b] Recorded in DMSO-d_6. [c] Recorded at ambient temperature. [d] Recorded at 40°.

The reason for the *syn*-phenyl isomer proton resonance being at lower field is more complex. In view of the fact that the difference in the uv spectra of benzaldehyde semicarbazone isomers (Figure 3) is less pronounced than that of either the two isomers of acetophenone or α-methyldeoxybenzoin semicarbazones, the implication is strong that both the ureido group and the third substituent on the imine group, *i.e.*, the hydrogen in this case, are instrumental in restricting the movement of the phenyl ring in the *syn*-phenyl isomers (VI). This is further implied by the fact that the H_α's are shielded in the *anti*-phenyl isomer of acetophenone semicarbazone, a measure of the interaction of the methyl group with the π orbitals of the aromatic ring. When the third substituent is small such as a hydrogen atom in the case of *syn*-phenyl benzaldehyde semicarbazone, the phenyl ring has less restriction to movement, and this allows more resonance interaction of the aromatic ring with the amine bond.

The photochemical conversion of *anti*-phenyl benzaldehyde semicarbazone into the *syn*-phenyl isomer is complicated by a competing side reaction. Products which incorporate solvent molecules are found in the reaction solution. This implies a second reaction pathway occurring where the imino hydrogen atom is lost to the medium.



V



VI

Experimental Section

The nmr spectra were done on an A-60 machine and the uv spectra were made using a Bausch and Lomb Spectronic 505. The melting points are uncorrected. The photochemical lamps used were 140 and 550-W medium-pressure Hanovia mercury arc lamps. The yields are corrected for recovered starting material.

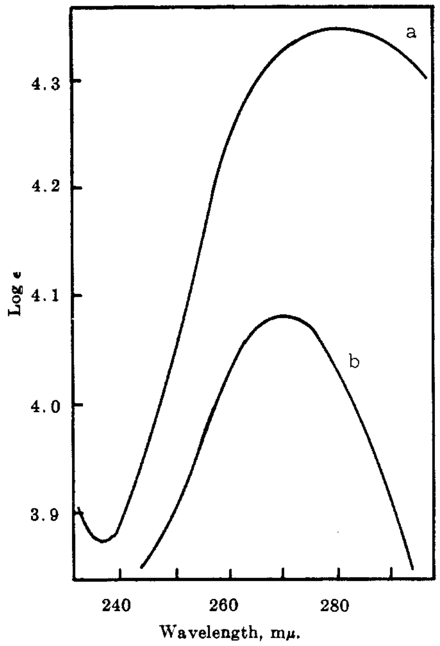


Figure 3.—The ultraviolet spectra of (a) the starting material and (b) the photoproduct of benzaldehyde semicarbazone.

Irradiation of Acetophenone Semicarbazone II in Tetrahydrofuran.—Acetophenone semicarbazone (5.0 g), mp 217–218°, in 200 ml of anhydrous tetrahydrofuran was placed in a quartz round-bottomed flask provided with a condenser and an inlet tube for nitrogen. The solution was deoxygenated for 5 min with a nitrogen stream and then irradiated with a 140-W mercury arc lamp for 24 hr. A white crystalline solid IV separated upon cooling which showed two spots on thin-layer chromatography. The solvent was carefully distilled off and the crystalline solid thus obtained also showed two spots on tlc. These two fractions were combined and continually extracted (24 hr) on a steam bath with a Soxhlet extracter using Skellysolve B as the solvent. The white solid that precipitated out from Skellysolve B was recrystallized from aqueous alcohol to give 2.3 g (85.1% yield), provided an analytical sample: mp 173.5–174.5°; λ_{max} (95% ethanol) 240 mμ (ε 12,640); ir (chloroform) 2.81, 2.94, and 5.94 μ. A corresponding dark reaction gave only recovered starting material.

Anal. Calcd for $C_9H_{11}N_3O$: C, 60.99; H, 6.26; N, 23.71. Found: C, 60.96; H, 6.31; N, 23.52; mol wt (by Rast method), 190.

Hydrolysis of Photoproduct IV from Acetophenone Semicarbazone.—The photoproduct (100 mg) was refluxed with 25 ml of 10% HCl for 1.5 hr. The solution was cooled and extracted several times with ether. After drying over anhydrous $MgSO_4$, the ether solution was evaporated to give a colorless liquid with an odor resembling that of acetophenone. It was recognized as acetophenone by comparing its retention time with an authentic sample by vpc.

To an alcoholic solution of the liquid was added a few drops of 2,4-dinitrophenylhydrazine solution. This resulted in the separation of an orange crystalline solid. It was filtered and washed with alcohol, mp 249–250°. Mixture melting point with the 2,4-dinitrophenylhydrazone of an authentic sample of acetophenone was undepressed.

Treatment of Photoproduct IV from Acetophenone Semicarbazone with Anhydrous Hydrogen Chloride.—The photoproduct (100 mg) was dissolved in 10 ml of anhydrous ethanol, and a gentle stream of anhydrous hydrogen chloride was bubbled through the solution. A white crystalline solid slowly settled out (0.5 min) which was filtered and washed with a few milliliters of aqueous alcohol, mp 200–201°. Mixture melting point with an authentic sample of acetophenone semicarbazone II was undepressed.

Irradiation of Benzaldehyde Semicarbazone in Tetrahydrofuran.—Benzaldehyde semicarbazone (3.0 g) in 200 ml of anhydrous tetrahydrofuran was irradiated for 24 hr with a 140-W lamp. The resulting solution showed two spots on tlc, one corresponding to the starting material. The filtrate was further concentrated and cooled in the refrigerator, and the precipitated solid was filtered. Partial melting occurred at about 140° and the semisolid resolidified. The latter crystals had mp 217-218°. The former crystals were dissolved in hot ethanol, and the first crop of crystals that separated out was shown to be a mixture by tlc. The second and third crops were shown to be pure by tlc. They were combined and dissolved in tetrahydrofuran to which Skellysolve B was added dropwise resulting in a precipitation of 0.5 g of a white solid (yield 71.4%). In a previously heated silicone oil bath a small sample of this solid in a capillary was introduced. It melted, then slowly resolidified, and melted at 217-218°: λ_{max} (95% ethanol) 275 mμ (ε 11,860); ir 2.87, 3.05, and 5.94 μ. A corresponding dark reaction produced only starting material.

Anal. Calcd for $C_8H_9N_3O$: C, 58.88; H, 5.82; N, 25.80. Found: C, 58.60; H, 5.69; N, 26.21.

The hydrolysis of the photoproduct of benzaldehyde semicarbazone with aqueous HCl to benzaldehyde and the isomerization of the initially prepared semicarbazone was accomplished in the same manner as described for acetophenone semicarbazone.

Preparation of the Two Semicarbazones of α-Methyldeoxybenzoin.—This was accomplished through the published procedures of Ramart-Lucas and Bruzau.[8]

Acetophenone Semicarbazone in Trifluoroacetic Acid.—Acetophenone semicarbazone (1.2 g) was dissolved in 10.4 g of trifluoroacetic acid. The solution was allowed to stand for 2 hr and then was poured into an ice-water mixture. The white precipitate was filtered immediately with a Büchner funnel, washed with an ice-sodium bicarbonate solution and later with water. The air-dried white solid melted at 194-197°. After recrystallization from 95% ethanol three times, it had the melting point of 201.5-202.0° and the mixture melting point with the starting material was undepressed.

Registry No.—Table I, **1**, 17539-52-5; Table I, **2**, 17539-53-6; Table I, **3**, 17539-54-7; Table I, **4**, 17539-55-8; Table I, **5**, 17539-56-9; Table I, **6**, 17539-57-0; Table I, **7**, 17539-58-1; Table I, **8**, 14066-73-0.

Acknowledgment.—The support of the National Science Foundation through its College Teacher Research Participation Program (P. A. B.), the High School Teacher Research Participation Program (D. B.), and the Undergraduate Research Participation Program (D. D. H.) is sincerely appreciated. We also gratefully acknowledge the aid of the National Science Foundation for the purchase of the nmr machine used in these experiments (Grant No. GP-3642).

Reactions of Ynamines

M. E. KUEHNE[1] AND P. J. SHEERAN

Department of Chemistry, University of Vermont, Burlington, Vermont 05401

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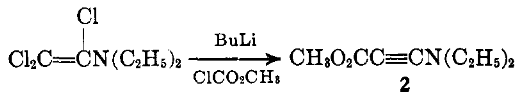
Reactions of ynamines with acidic carbon compounds such as malononitrile and ethyl cyanoacetate gave cyanoenamines, whereas acidic nitrogen compounds such as arylsulfonamides gave saturated amidines. The condensation of several arylsulfonylimides with ynamines and electrocyclic opening of the adducts led to unsaturated amidines while 2-pyridal-*p*-toluenesulfonimide gave a pyrrocoline. Reactions of diphenylketene and dimethylketene with ynamines furnished aminocyclobutenone and four-membered cyclic enol ether products. Similarly, sulfenes and ynamines formed cyclic sulfones. Aryl isocyanates and ynamines gave 4-amino-2-quinolones and 2-amino-4-quinolones. An example of a 1,3 dipolar addition and a reaction with tetraphenylcyclopentadienone, which gave a pentaphenylaniline, are also described.

Ynamine chemistry has been investigated only in the last 4 years and remains largely unexplored. During the course of our studies in this area, preparative methods for this new class of compounds became available,[2-8] and some reactions of these compounds were described.[9-11] This report presents further aspects of ynamine chemistry.

Two of the ynamines used in this work have not been described previously. N,N-dipropylheptynylamine (1) was prepared by a displacement reaction from an acetylenic ether,[5] whereas N,N-diethylcarbomethoxyethynylamine (2) was obtained from N,N-diethyltrichlorovinylamine, butyllithium, and methyl chlorocarbonate.

$$\mathrm{CH_3(CH_2)_4C{\equiv}COC_2H_5} \xrightarrow{\mathrm{(C_3H_7)_2NLi}} \mathrm{CH_3(CH_2)_4C{\equiv}CN(C_3H_7)_2}$$

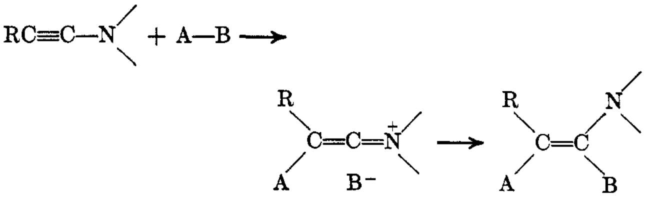
1



$$\mathrm{Cl_2C{=}\overset{Cl}{C}N(C_2H_5)_2} \xrightarrow[\mathrm{ClCO_2CH_3}]{\mathrm{BuLi}} \mathrm{CH_3O_2CC{\equiv}CN(C_2H_5)_2}$$

2

Since electrophilic substitution adjacent to a carboxyl group often presents a serious synthetic obstacle, formal activating derivatives of carboxylic acids, such as ynamines, are of potential synthetic interest. However, ynamines do not parallel enamines in their broad utility for substitution reactions.[12] In contrast to the formation of aliphatic imonium salts, which one obtains on nucleophilic reactions of enamines, energetically less favorable allenic imonium functions are generated by electrophilic attack on ynamines. Thus one can expect ynamines to be less reactive toward monofunctional electrophiles than enamines and to undergo preferentially reactions in which addition takes place at positions α and β to the nitrogen. Ynamines should thus be good substrates for reactions with di-



favored product

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[1] Alfred P. Sloan Fellow.

[2] H. G. Viehe, *Angew. Chem.*, **75**, 638 (1963).

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