

Anal. Calcd for $C_{10}H_{12}O_2Cl_2$: C, 51.09; H, 5.14. Found: C, 51.34; H, 5.25.

Cyclization of 9e to 5,7-dichloro-4-methyl-2,3-dihydrobenzofuran (7). The ethanol derivative **9e** (0.5 g) was refluxed for 6 hr in a mixture of 12 ml of 48% hydrobromic acid and 20 ml of acetic acid. The hot solution was poured on ice and extracted with three 150-ml portions of ether. The combined ether extracts were washed with two portions of 10% sodium hydroxide and once with cold water. The ether portion was dried, the ether was removed *in vacuo*, and the residue was sublimed, yielding 0.25 g of product, mp 108–110°. All of the spectral properties, including the mass spectrum, were in agreement with the dihydrobenzofuran structure **7**.

Equilibrations in D_2SO_4 and H_2SO_4 . These were carried out in general as described.² For D_2SO_4 runs, about a 1:4 (v/v) ratio of compound to acid was used. For H_2SO_4 runs at varying temperatures, about 1 g of compound per 12–15 ml of acid was used. After the desired time, the sample or an aliquot was quenched in water, extracted with ether, and dried, solvent was removed, and the sample was analyzed by vpc or mass spectrometry. The recovery of material in H_2SO_4 was around 75%, using the *cis* or *trans* compounds **2** and **3**. With the 2,2-dimethyl compound **4** and D_2SO_4 , from 0.6 g of sample in 5 g of D_2SO_4 , 42% of crystalline **4** was recovered, after two crystallizations from petroleum ether, using a Dry Ice-acetone bath.

For nmr determinations, a sample was weighed accurately and dissolved in a known volume of CCl_4 .

The accuracy of the mass spectral deuterium determinations was about $\pm 2\%$; the reproducibility of mass spectral runs on the same sample was $\pm 1\%$ or better. The nmr runs were reproducible on the same sample, and probably accurate within $\pm 3\%$. The vpc analyses for the *cis* and *trans* compounds were accurate to $\pm 2\%$ or better; the methyl-rearranged product **4** was not completely resolved from the *trans* compound **3**, and for small amounts of **4** and large amounts of **3**, as in Table II, the accuracy of determining **4** is much lower. The vpc separations were done using 25% Ucon Polar columns.

Registry No.—**2**, 1876-14-8; **3**, 1876-13-7; **4**, 6834-35-1; **5**, 6834-34-0; **6**, 2030-78-6; **7**, 52259-73-1; **8c**, 1201-79-2; **9b**, 52259-74-2; **9c**, 52259-75-3; **9d**, 52259-76-4; **9e**, 52259-77-5; D_2SO_4 , 13813-19-9; H_2SO_4 , 7664-93-9; 2,4-dichloro-5-methylphenol, 1124-07-8; allyl bromide, 106-95-6.

References and Notes

- (1) We are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.
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- (8) For complications due to the presence of excess SO_3 in some samples of D_2SO_4 , see Experimental Section.
- (9) R. E. Rindfusz, P. M. Ginnings, and V. L. Harnack, *J. Amer. Chem. Soc.*, **41**, 665 (1919); **42**, 157 (1920).
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- (13) Reference 7b, p 204.
- (14) P. T. Lansbury and F. F. Hilfiker, *Chem. Commun.*, 619 (1969); P. T. Lansbury, *Accounts Chem. Res.*, **5**, 313 (1972).
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- (16) Elemental analyses were by Galbraith Laboratories. Mass spectra were obtained on an LKB mass spectrometer; vpc analyses were done on a Varian Aerograph 90-P instrument, and nmr spectra were determined in CCl_4 solution, using a Varian A-60 or a Jeolco 100 spectrometer. All melting points and boiling points are uncorrected. We are indebted to Dr. James R. Fehner for assistance with the mass spectral and nmr determinations.
- (17) R. G. Parker, *J. Soc. Chem. Ind.*, **36**, 692 (1917).
- (18) This was worked out by Professor S. M. Hecht, of the Department of Chemistry at Massachusetts Institute of Technology, then an undergraduate at the University of Rochester.

Synthesis and Dehydrogenation of α -(9-Acridanyl)acetonitriles

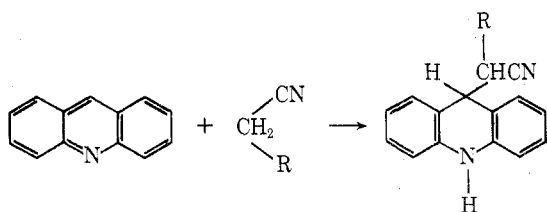
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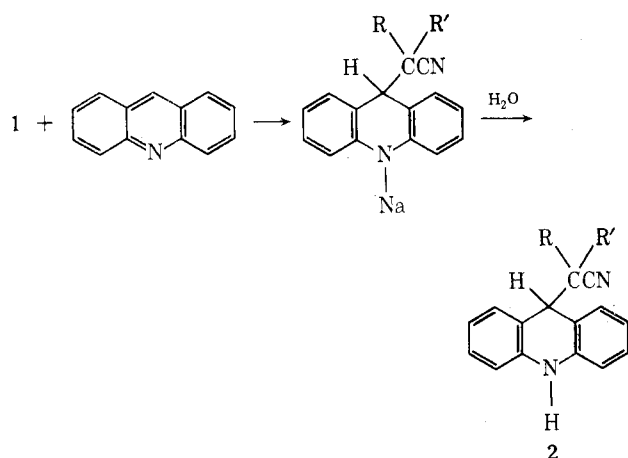
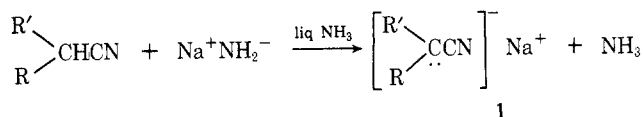
Four α -(9-acridanyl)acetonitriles [$9-(C_{13}H_{10}N)CRR'CN$] were synthesized by the 9,10 addition of the anions (prepared using sodium amide) of the nitriles $RR'HCCN$ ($R = R' = H$; $R = H, R' = CH_3$; $R = CH_3, R' = CH_3$; and $R = H, R' = C_6H_5$) to acridine. Two of these products ($R = R' = H$ and $R = H, R' = C_6H_5$) were dehydrogenated to give exclusively the corresponding 9-cyanomethyleneacridans and a third ($R = H, R' = CH_3$) was dehydrogenated to give a mixture α -(9-acridinyl)propionitrile (major product) and α -cyano- α -methyl-9-methyleneacridan (minor product). The fourth compound ($R = R' = CH_3$) could not be dehydrogenated apparently for steric reasons.

Kröhnke and Honig¹ found that very active methylene compounds undergo noncatalytic 9,10 addition to acridine to give 9 substituted acridans. Since several years ago² we effected the 9,10 addition of sodio ketones to acridine to give α -(9-acridanyl) ketones which on dehydrogenation



gave α -(9-acridanyl) ketones, it was decided to extend this work to the synthesis of α -(9-acridanyl)acetonitriles, **2**. The sodium derivatives of acetonitrile ($R = R' = H$), propionitrile ($R = H, R' = CH_3$), isobutyronitrile ($R = R' = CH_3$), and phenylacetonitrile ($R = H, R' = C_6H_5$) added to acridine to give 78.5%, 76.5%, 49.5%, and 87.0% yield of the corresponding acridanylacetonitriles, **2**. Phenylacetonitrile, the most reactive of the nitriles, failed to react under Kröhnke and Honig's noncatalytic conditions.

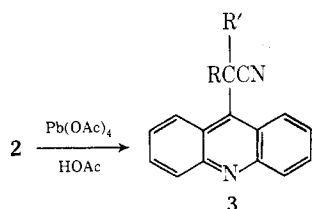
In all but one case, the only reaction products isolated were the α -(9-acridanyl)acetonitriles. With acetonitrile, in addition to 9-cyanomethyleneacridan (78.5%), there was obtained 10% of the dehydrogenated compound α -cyano-9-



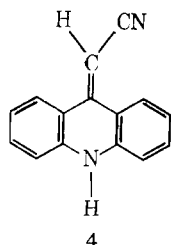
methyleneacridan (the tautomer of 9-cyanomethylacridine, *vide infra*); the aeration of alkaline suspensions of acridans is a well known method of dehydrogenating certain acridans to acridines.³

In the phenylacetonitrile reaction, some of the product (3.8%) was isolated as the 1:1 adduct of α -(9-acridanyl)phenylacetonitrile and acridine. This adduct could be recrystallized from benzene and melted sharply (139–141°). Its infrared spectrum differed from that of a mechanical mixture of α -(9-acridanyl)phenylacetonitrile and acridine. Its elemental analysis and its quantitative separation (by means of dilute hydrochloric acid) into acridine and α -(9-acridanyl)phenylacetonitrile showed that it consisted of 1:1 molar combination of the latter two compounds.

Three of the nitriles, 2, were dehydrogenated using lead tetraacetate as the oxidizing agent.



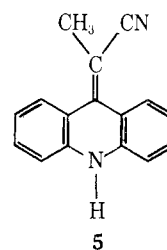
With 9-cyanomethylacridan (2, R = R' = H), a 55.5% yield of dehydrogenated product was obtained. Although its elemental analysis and melting point agree with those reported⁴ in the literature for 9-cyanomethylacridine, its infrared spectrum (*vide infra*) indicate that it exists in its tautomeric acridan structure, 4. Thus, the reported⁴ syn-



thesis of 9-cyanomethylacridine from the interaction of the lithium derivative of 9-methylacridine with *N*-methyl-*N*-cyanoaniline does not give 3 (R = R' = H) but rather its tautomer, 4.

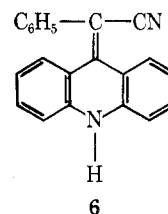
The lead tetraacetate oxidation of α -(9-acridanyl)propionitrile (2, R = H, R' = CH₃) gives a 49.5% yield of a mixture which initially consisted of α -(9-acridanyl)propi-

onitrile (3, R = H, R' = CH₃, 41%) and its tautomer, α -cyano- α -methyl-9-methyleneacridan, 5, 8.5%. The fact that



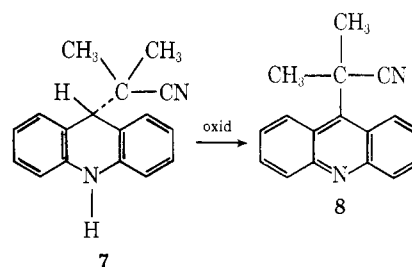
these two tautomers were isolated in a pure state by crystallization is somewhat unusual since tautomers do not, as a rule, readily lend themselves to such an easy separation. Compound 5 is more stable than its tautomer (3, R = H, R' = CH₃) since the latter was quantitatively converted to the former on standing 6 months at room temperature or by heating it for a short period of time above its melting point. Thus, 5 is the thermodynamic product and its tautomer is the kinetic product.

The dehydrogenation of α -(9-acridanyl)phenylacetonitrile (2, R = H, R' = C₆H₅) gave exclusively α -cyano- α -phenyl-9-methyleneacridan, 6, as shown by ir analysis (*vide*



infra) and none of its expected tautomer, α -(9-acridanyl)- α -phenylacetonitrile (3, R = H, R' = C₆H₅). The melting point agrees with that of the material obtained by Mizuno, *et al.*,⁵ from the reaction of phenylacetonitrile with 9-chloroacridine using sodium amide as the condensing agent. However, these workers did not establish its structure. Based on our studies, there is very little doubt that they also obtained α -cyano- α -phenyl-9-methyleneacridan, 6.

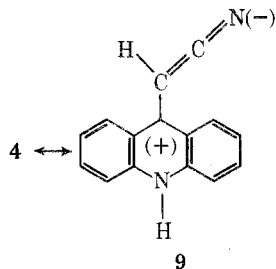
The attempted dehydrogenation of α -(9-acridanyl)isobutyronitrile, 7, using both lead tetraacetate and acidic ferric chloride failed; the only identifiable product was acridine. This failure appears to be due to steric reasons. Thus, since the 9-carbon atom is in a tetrahedral configuration in 7, the acridan ring is not planar and the bulky tertiary isob-



utyronitrile group can lie on the relatively unhindered side of the bent acridan molecule. However in 8, the 9-carbon atom is now part of the planar acridine ring and contains the planar sp² bonding orbitals. Thus, the tertiary, α -carbon of the isobutyronitrile group must necessarily lie in the same plane as the acridine ring in 8. The steric hindrance of the 1,8-hydrogen atoms of the acridine ring appear to prevent this from happening with the bulky isobutyronitrile group.

The N-H band at *ca.* 2.91–3.05 μ and the strong C \equiv N band at 4.52–4.54 μ support the α -cyano-9-methylene structure for the 9-(=CRCN) acridans. By contrast, the

C≡N absorption for the 9-CHRCN compounds is weak and appears at 4.40–4.47 μ . The increase in wavelength for the C≡N group in the α -cyano-9-methylene compounds is expected considering a resonance contribution from **9**. This would also be consistent with the increase in wavelength of the N–H group of these compounds as compared with acridine itself.⁶



Experimental Section

Synthesis of α -(9-Acridanyl)nitriles by the 9,10 Addition of Sodianitriles to Acridine. 1. 9-Cyanomethylacridan. To a stirred suspension of sodium amide (0.2 mol, from 4.6 g of sodium) in 200 ml of liquid ammonia was added acetonitrile (0.2 mol, 8.2 g) in an equal volume of anhydrous ether over a 5-min period. After stirring the mixture for 20 min, powdered acridine (0.2 mol, 35.8 g) was added using about 35 ml of anhydrous ether to wash the last traces of acridine into the reaction mixture. After 6.5 hr of stirring, the last traces of acridine dissolved and then 120 ml of anhydrous ether was added. The ammonia was allowed to evaporate overnight. Then, water (75 ml) was added and the hydrolyzed reaction filtered. The solid product was washed with water and ether to give 38.0 g of material, mp 164.5–174°. Its ir spectrum showed that it consisted of a mixture of 9-cyanomethylacridan and α -cyano-9-methyleneacridan.

The water-ether filtrate (*vide supra*) was separated into its phases and the aqueous phase was discarded. The ether layer was washed with three 75-ml portions of water, dried over calcium chloride, and concentrated to about 65 ml. After standing at –5° overnight, the crystalline product was filtered, washed with ether, and dried to give an additional 4.1 g of product, mp 179–182° which had an infrared spectrum identical with that of the mixture described above. The combined products were boiled in 3 l. of benzene, filtered, and cooled to room temperature. The small amount of insoluble material was discarded. The benzene solution was extracted with three 100-ml portions of 6 *N* hydrochloric acid, washed with three 100-ml portions of water, and dried over calcium chloride. The solvent was evaporated to give 34.5 g (78.5%) of 9-cyanomethylacridan, mp 187–189° from benzene-heptane.

Anal. Calcd for C₁₅H₁₂N₂: C, 81.82; H, 5.45; N, 12.73. Found: C, 82.09; H, 5.75; N, 12.64.

Ir spectrum; weak C≡N band at 4.42 μ , a sharp N–H bond at 2.84 μ , and characteristic acridan bands at 6.26, 6.33, 7.66, 13.10, 13.27, and 14.56 μ .

The combined aqueous extracts from above were made basic with aqueous ammonia. The solid, free base which was liberated was filtered, washed with water, and dried to give α -cyano-9-methyleneacridan (10.0%, mp 230–231.5° from benzene); the same material, mp 227–228°, is called 9-cyanomethylacridine in the literature.⁴

Anal. Calcd for C₁₅H₁₀N₂: C, 82.54; H, 4.62; N, 12.84. Found: C, 82.40; H, 4.82; N, 13.25.

Ir spectrum: Strong, sharp C≡N at 4.54 μ , N–H band in the 2.95–3.05- μ region, a strong conjugated double bond type band at 6.14 μ , and three aromatic bands 6.28, 13.59, and 14.55 μ .

2. α -(9-Acridanyl)phenylacetoneitrile. The above procedure was employed using phenylacetoneitrile (0.2 mol, 23.4 g). After the acridine was added, the mixture was stirred for 3 hr. Most of the acridine was still undissolved but it all went into solution when 100 ml of anhydrous ether was added and the mixture was stirred for an additional 30 min. An additional 50 ml of anhydrous ether was added and the ammonia was allowed to evaporate. After adding water (75 ml), the hydrolyzed mixture was filtered. The solid thus obtained was washed with water and ether and, after drying, consisted of 36.3 g of α -(9-acridanyl)- α -phenylacetoneitrile, mp 176–178° from benzene.

The phases of the aqueous ether filtrate from above were sepa-

rated. The ether layer was washed with three 70-ml portions of water and dried over calcium chloride. It was concentrated to 90 ml and allowed to crystallize. The crystals were filtered, washed with ether, and dried to give an additional 12.9 g of α -(9-acridanyl)phenylacetoneitrile, mp 176–178°, for a total of 49.2 g (83%) of this product.

Ir spectrum: an N–H band at 2.84 μ , a weak C≡N band at 4.40 μ , and several aromatic bands.

Anal. Calcd for C₂₁H₁₆N₂: C, 85.10; H, 5.44; N, 9.45. Found: C, 85.44; H, 5.71; N, 9.60.

The ether filtrate from above was concentrated to 40 ml and allowed to crystallize at room temperature. There was obtained 3.7 g of yellow crystals, mp 139–141° from ether. Its ir spectrum differed from that of pure α -(9-acridanyl)phenylacetoneitrile and that of a mechanical mixture of this acridanyl nitrile with acridine.

Anal. Calcd for C₃₄H₂₅N₃ (a 1:1 adduct of acridine and α -(9-acridanyl)phenylacetoneitrile): C, 85.90; H, 5.26; N, 8.84. Found: C, 85.75; H, 5.33; N, 8.98.

It showed a weak C≡N band at 4.46 μ , an N–H-type bond at 3.10 μ , and several aromatic bands. A sample (0.54 g) was dissolved in ether and extracted with dilute hydrochloric acid. The ether solution was then washed with water, dried over calcium chloride, and ether evaporated to give 0.34 g (0.0011 mol) of α -(9-acridanyl)phenylacetoneitrile as indicated by its ir spectrum and mixture melting point with an authentic sample. The acidic aqueous extracts and aqueous washings were combined and treated with 10% aqueous potassium hydroxide to liberate the free base, which was filtered, washed with water, and dried to give 0.20 g (0.0011 mol) of acridine as indicated by its ir spectrum and a mixture point with an authentic sample.

The 3.7 g (3.8%) of the adduct contains an additional 2.3 g of α -(9-acridanyl)phenylacetoneitrile and the total yield of this product is 87%. The remaining ether filtrate from the reaction mixture from which the 3.7 g of adduct was obtained, was stripped of solvent to give 6.3 g of an orange semisolid. This material was pressed on a fritted-glass filter to give 2.9 g (0.016 mol) of acridine as indicated by a mixture melting point with an authentic sample and 3.2 g of a dark colored oil which was shown (ir spectrum) to consist mostly of unreacted phenylacetoneitrile and containing some dissolved acridine and α -(9-acridanyl)phenylacetoneitrile.

From the analogous reaction with propionitrile, there was obtained α -(9-acridanyl)propionitrile (76.5%, mp 115–116° from benzene-heptane).

Anal. Calcd for C₁₆H₁₄N₂: C, 82.05; H, 5.98; N, 11.97. Found: C, 82.23; H, 5.96; N, 11.96.

The isobutyronitrile reaction gave α -(9-acridanyl)isobutyronitrile, mp 194–195° (sealed tube).

Anal. Calcd for C₁₇H₁₆N₂: C, 82.26; H, 6.45; N, 11.29. Found: C, 82.25; H, 6.56; N, 11.33.

Dehydrogenation of α -(9-Acridanyl)nitriles. 1. Dehydrogenation of α -(9-Acridanyl)acetoneitrile. Lead tetraacetate (4.0 g, 0.009 mol) containing acetic acid (1.6 g) was added slowly at room temperature to a stirred solution of α -(9-acridanyl)acetoneitrile (2.0 g, 0.009 mol) in 300 ml of benzene containing 1.3 ml of pyridine. After stirring at room temperature for 1 hr, the lead salts were filtered; the benzene filtrate was washed with four 100-ml portions of water and was dried over calcium chloride. The dried benzene solution was concentrated to about 180 ml and 50 ml of heptane was added. The resulting solution was concentrated to 90 ml and allowed to crystallize at room temperature overnight. The filtered crystals were washed with benzene and dried to give 0.84 g of α -cyano-9-methyleneacridan, mp 230.0–231.5°⁴ from benzene.

The benzene-heptane filtrate from above was extracted with three 30-ml portions of 6 *N* hydrochloric acid, washed with water, and dried over calcium chloride. The solvents were evaporated to give 0.9 g of an acid-insoluble residue which was shown by its ir spectrum to consist mainly of recovered α -(9-acridanyl)acetoneitrile.

The acidic aqueous extracts and washings from above were combined and treated with aqueous ammonia to liberate the free base which was filtered, washed with water, and dried to give 0.27 g of additional α -cyano-9-methyleneacridan, mp 230.0–231.5°⁴ from benzene. The two samples of this material were shown, by an ir spectrum and the nondepression of a mixture melting point, to be identical with the compound which was obtained as a side product in the preparation of 9-cyanomethylacridine (*vide supra*). A total of 1.11 g (55.5%) of product was obtained.

2. Dehydrogenation of α -(9-Acridanyl)propionitrile. A mixture of α -(9-acridanyl)propionitrile (4.7 g, 0.02 mol), 250 ml of benzene, 2.6 ml of pyridine, lead tetraacetate (8.8 g, 0.02 mol), and

2.4 g of acetic acid was treated as described in the last experiment up to the point of drying the reaction mixture over calcium chloride. The dried solution was evaporated to give 2.2 g of a viscous residue, whose ir spectrum showed that it consisted of unreacted α -(9-acridanyl)propionitrile and some unknown carbonyl-containing materials.

The acidic aqueous extracts and washings from above were treated with aqueous ammonia to liberate the free base which was filtered, washed with water, and dried to give 3.0 g of a mixture of two compounds, mp 50–90°. Repeated crystallization of this mixture from ether–petroleum ether gave 1.9 g (41%) of α -(9-acridinyl)propionitrile (A), mp 115.5–117° (yellow crystals from heptane containing a small amount of pyridine), and 0.4 g (8.5%) of α -cyano- α -methyl-9-methyleneacridan (B), mp 197–199° from ether–petroleum ether.

Anal. of A. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.81; H, 5.39; N, 12.38. *Anal.* of B. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.35; H, 5.18; N, 11.97.

The ir spectrum of A showed a weak C \equiv N band at 4.43 μ and a strong aromatic band at 13.27 μ . There were no N–H bands present and there was no absorption in the 6.0–6.2- μ region. The ir spectrum of α -cyano- α -methyl-9-methyleneacridan (B) showed an N–H band at 2.96 μ , a strong C \equiv N band at 4.52 μ , a strong, sharp band at 6.20 μ (indicative of a conjugated double bond), and various aromatic bands.

Heating A briefly above its melting point converted it quantitatively to B. This conversion also occurred when A was kept at room temperature for 6 months. These conversions were verified from their ir spectra and melting points.

3. Dehydrogenation of α -(9-Acridanyl)phenylacetonitrile.

Lead tetraacetate (8.8 g, 0.02 mol) containing acetic acid (2.6 ml) was added slowly at room temperature to a stirred solution of α -(9-acridanyl)phenylacetonitrile (5.9 g, 0.02 mol) in 300 ml of benzene. After stirring at room temperature for 1 hr, the lead salts were filtered and the benzene filtrate was washed with four 100-ml portions of water and was dried over calcium chloride. The benzene solution was concentrated to 80 ml and was diluted with 250 ml of ether. The resulting solution was extracted with three 100-ml portions of 6 N hydrochloric acid and was then washed with four 100-ml portions of water. After drying over calcium chloride, the solvents were evaporated to give 3.2 g of a residue, mp 45–200°; its ir spectrum showed that it contained unreacted α -(9-acridanyl)phenylacetonitrile and some unknown materials containing carbonyl functions which were not characterized further.

The combined acidic aqueous extracts and washings from above were treated with aqueous ammonia to liberate the free base which separated as an oil. This product was dissolved in ether and, after washing with water and drying (calcium chloride), the ether was evaporated to give 2.7 g of reddish, gummy solid, mp 35–55°; its ir spectrum showed an N–H band at 2.91 μ , a strong C \equiv N band at 4.53 μ , and various aromatic bands and agrees with the structure of α -cyano- α -phenyl-9-methyleneacridan. The very crude product was repeatedly recrystallized from benzene–petroleum ether to give 0.5 g (7.5%) of pure α -cyano- α -phenyl-9-methyleneacridan, mp 209.5–210.5° [literature value for α -(9-acridinyl)- α -phenylacetonitrile, 210°⁴].

Anal. Calcd for $C_{21}H_{14}N_2$: C, 85.69; H, 4.79. Found: C, 85.65; H, 5.08.

Its ir spectrum was identical with that described above.

The dehydrogenation of α -(9-acridanyl)propionitrile gave a mixture of two products. (a) α -Cyano- α -methyl-9-methyleneacridan (8.5%, mp 197–199° from ether–petroleum ether). *Anal.* Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.35; H, 5.18; N, 11.97. (b) α -(9-Acridinyl)propionitrile (41% 115.5–117° from heptane). *Anal.* Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.81; H, 63.9; N, 12.58.

Registry No.—2 (R = R' = H, 22409-47-8; 2 (R = H; R' = C_6H_5), 52673-98-0; 2 (R = H; R' = CH_3), 52673-99-1; 2 (R = H; R' = CH_3), 52674-00-7; 3 (R = H; R' = CH_3), 52674-01-8; 4, 52674-02-9; 5, 52674-03-0; 6, 52674-04-1; 7, 52674-05-2; acridine, 260-94-6; acetonitrile, 75-05-8; phenylacetonitrile, 140-29-4; propionitrile, 107-12-0; isobutyronitrile, 78-82-0.

References and Notes

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Certain Condensations Effected by 2,6-Dimethoxyphenyllithium

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2,6-Dimethoxyphenyllithium (2,6-DMPL) can be acylated with several aromatic and heterocyclic esters to give ketones. The use of methyl isonicotinate gave 2,6,2',6'-tetramethoxydiphenylcarbinol and no ketone. Methyl anisate and 2,6-DMPL gave a mixture of 2,6,4'-trimethoxybenzophenone and 4-(2,6,2',6'-tetramethoxydiphenylmethylene)-2,5-cyclohexadienone. Several aliphatic esters were used to give ketones, carbinols, or a mixture of the two. With the three esters, ethyl acetate, ethyl propionate, and ethyl phenylacetate, which contain α -hydrogen atoms, small amounts of β -keto esters (for the first two esters) or the ketonic cleavage product of the β -keto ester (for the third ester) were formed. While 2-picoline, 4-picoline, and methylpyrazine can be benzoylated using 2,6-DMPL at their methyl groups with methyl benzoate, this reaction fails with 3-picoline and 2,6-dimethoxybenzophenone is formed.

Resorcinol dimethyl (RDME) was first metalated by Wittig and Pockels¹ by reaction with phenyllithium at room temperature for 60 hr to give 2,6-dimethoxyphenyllithium (2,6-DMPL) which was treated with gaseous carbon dioxide to give a mixture of 2,6,2',6'-tetramethoxybenzophenone (25%) and 2,6-dimethoxybenzoic acid (20%). Several other condensations have been effected with 2,6-DMPL including its reaction (1) with *N*-methylformanilide² to give 2,6-dimethoxybenzaldehyde (55%); (2) with

benzophenone³ to give 2,6-dimethoxydiphenylcarbinol; (3) with a series of α,ω -dibromoalkanes to give α,ω -bis(2,6-dimethoxyphenyl)alkanes⁴ (50–90%); (4) with aliphatic and aromatic nitro compounds⁵ to give a series of nitroxides; and (5) with the sterically hindered ketone 2,6,2',6'-tetramethoxybenzophenone⁶ to give 2,6,2',6',2'',6''-hexamethoxytriphenylcarbinol in 77.8% yield.

Of particular interest in connection with the present problem (*vide infra*) is the work of Limaye and coworkers