[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND PHARMACEUTICAL CHEMISTRY, MEDICAL COLLEGE OF VIRGINIA]

α-Aminoalkanesulfonic Acids[1,2]

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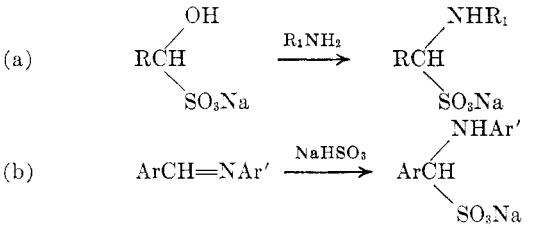
Various α-aminoalkanesulfonic acids and some of their derivatives were prepared to facilitate a study of their biological properties. This offered an opportunity to make a more thorough study of their chemical properties and reactions. Practical syntheses are described. The behavior of the amino sulfonic acids towards oxidizing agents and toward phenylhydrazine and semicarbazide are analogous to those of aldehyde. They form sulfonanilides. Their reaction with cyanide and with active methylene compounds is considered essentially an alkylation; the alkylation may proceed with elimination of the sulfonic acid group or with replacement of the amino group.

α-Amino sulfonic acids, analogs of amino acids in which the carboxyl group is replaced by a sulfonic acid group, have received limited study from the biological scientist, *e.g.*, for anticancer activity[3,4] and for antiviral properties.[5,6] Therefore, the present study was undertaken to make available a series to permit systematic study of their antitumor activity and any possible antagonism to the natural amino acids. In the Tables are listed some of the compounds prepared. *In vivo* studies are under way in the laboratories of Irvin and Wilson,[7] who are reporting their results elsewhere.

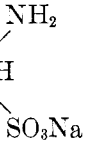
α-Aminoalkanesulfonic acids have been known for more than fifty years[8,9]; but many of their interesting properties have not been previously described.

The synthesis may proceed in either of two ways, indicated as follows:



Reaction a is generally applicable and may be employed with aliphatic or aromatic aldehydes, and the amine may be aliphatic or aromatic or even ammonia; equimolar amounts of aldehyde and bisulfite are stirred together in water, forming the aldehyde-bisulfite *in situ*, followed by an equimolar amount of amine; the reaction proceeds at room temperature but may be facilitated by warming. Reaction b has thus far been employed only with aromatic reagents, affording excellent yields for the most part.

The salts are stable in aqueous solution even up to about 70°. They decompose in boiling water, and they are unstable in the presence of alkali. They are stable to acid, as was noted by Backer.[10]



Primary amino derivatives of structure

in hydrochloric acid *p*H = 2 afford good yields of the corresponding sulfonic acid.

The α-aminoalkanesulfonates show many reactions characteristic for aldehydes. They reduce Tollen's and Fehling's solutions; they decolorize solutions of permanganate, of dichromate, and of iodine–potassium iodide. (The aldehyde-bisulfite complex does not reduce iodine.[11]) They react readily with phenylhydrazine or semicarbazide to give good yields of the phenylhydrazone or semicarbazone, respectively, of the aldehyde employed in preparing the sulfonic acid. The speed with which these derivatives precipitate suggests their formation directly from the sulfonate.

The infrared spectra show characteristic bands for the —SO_3Na and —NHR groups and no presence of bisulfite or sulfite. Further studies are in progress.

An aqueous solution of sodium α-aminophenylmethanesulfonate, XI, stirred at room temperature with an equivalent of aniline slowly forms crystals of the less soluble α-anilinophenylmethanesulfonate (XII), showing that an amine exchange can occur under these conditions. This type of reaction requires further study before we can say how widely it may be applied.

An arylaminoalkanesulfonate in boiling water undergoes rearrangement which suggests the reaction

(1) Number 20 in Amino Acids series. For No. 19 see D. A. Coviello and W. H. Hartung, *J. Org. Chem.*, 1611.

(2) Supported by Public Health Service Grant Cy-3024, National Institutes of Health. For this support the authors are grateful.

(3) H. McIlwain, *J. Chem. Soc.*, 75 (1941).

(4) D. M. Greenberg and M. P. Schulman, *Science*, **106**, 271 (1947).

(5) W. W. Ackerman, *Proc. Soc. Exptl. Biol. Med.*, **80**, 362 (1952).

(6) R. L. Thompson, *J. Immunol.*, **55**, 345 (1947).

(7) J. L. Irvin and J. Wilson, University of North Carolina, S. E. Regional Meeting, Am. Chem. Soc., Richmond, Nov. 5, 1959.

(8) E. Knoevenagel, *Ber.*, **37**, 4087 (1904).

(9) H. Bucherer and A. Schwalbe, *Ber.*, **39**, 2810 (1906).

(10) H. J. Backer and H. Mulder, *Rec. trav. chim.*, **53**, 1120 (1934).

(11) Ripper, *Monatsh.*, **21**, 1079 (1900) through C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, New York, 1944, p. 127.

TABLE I

$$R-\underset{\displaystyle NHR'}{\overset{\displaystyle |}{CH}}-SO_3Na$$

α-AMINOALKANE SULFONATES

No.	—R	—R′	Softening Point	Crystals from	Yield, %	Nitrogen Calcd.	Nitrogen Found	Remarks
I	H-	H-	—	Water	60	—	—	[a]
II	H-	CH_3	—	Water	60	—	—	[a]
III	H-	Et_2-	—	Water	70	—	—	[a]
IV	H-	C_6H_5-	—	Water-alcohol	90	—	—	[a]
V	n-C_3H_7-	H-	—	Water	70	—	—	[c]
VI	n-C_3H_7-	C_6H_5-	108–110	Alcohol	85	5.59	5.7	
VII	i-C_3H_7-	H-	—	Water	65	—	—	[c]
VIII	i-C_3H_7-	C_6H_5-	110–112	Alcohol	80	5.59	5.8	
IX	i-C_4H_9	H-	—	Water	70	—	—	[c]
X	i-C_4H_9	C_6H_5-	118–120	Alcohol	80	5.28	5.15	
XI	C_6H_5-	H-	—	Water	75	—	—	[c]
XII	C_6H_5-	C_6H_5-	115–117	Alcohol	90	4.91	4.8	
XIII	C_6H_5-	p-$CH_3C_6H_4$-	138–140	Alcohol	95	4.68	4.72	
XIV	C_6H_5-	p-ClC_6H_4-	178–180	Alcohol	95	4.6	4.32	[b]
XV	C_6H_5-	p-C_6H_4COONa	—	Water	70	4.0	3.8	
XVI	C_6H_5-	p-$C_6H_4SO_3Na$	—	Water	65	—	—	[a]
XVII	C_6H_5-	C_5H_{10}-	—	Water	70	—	—	[a]
XVIII	p-ClC_6H_4-	H-	—	Water	90	5.76	5.5	
XIX	p-ClC_6H_4-	C_6H_5-	145–147	Alcohol	95	4.37	4.31	
XX	$C_6H_5CH_2$-	H-	—	Water	80	—	—	
XXI	$C_6H_5CH_2CH_2$-	H-	—	Water	85	5.95	5.82	
XXII	$C_6H_5CH_2CH_2$-	C_6H_5-	95–96	Alcohol	90	4.5	4.32	

[a] Properties of these compounds agree with those reported by Knoevenagel.[8] [b] $C_{13}H_{11}NO_3ClNa$ requires, N, 4.6; S, 8.96; Found, N, 4.32; S, 9.06.[17] [c] The compounds were converted to the corresponding aminonitriles; their melting points agreed well with the reported values. The free acids from the salts compared well with those reported by McIlwain.[3]

TABLE II

$$R-\underset{\displaystyle NHAr}{\overset{\displaystyle |}{CH}}-SO_2NHAr$$

ARYLAMIDES OF α-ARYLAMINOALKANE SULFONIC ACIDS

No.	R—	Ar—	M.P. (Dec.)	Crystals from	Yield, %	N, % Calcd.	N, % Found	Remarks
XXIII	n-C_3H_7-	C_6H_5-	123–124	Alcohol	80	9.2	9.34	
XXIV	i-C_3H_7-	C_6H_5-	120–121	Water	75	—	—	[d]
XXV	n-C_4H_9-	C_6H_5-	125–126	Water	75	8.76	8.79	
XXVI	i-C_4H_9	C_6H_5-	128–129	Water	80	—	—	[dd]
XXVII	C_6H_5-	C_6H_5-	125–126	Alcohol	85	—	—	[e]
XXVIII	C_6H_5-	p-$CH_3C_6H_4$-	117–118	Alcohol	90	—	—	[f]
XXIX	C_6H_5-	p-ClC_6H_4-	133–134	Alcohol	95	6.87	6.62	
XXX	C_6H_5-	p-C_6H_4COONa	—	Water	80	5.96	5.80	
XXXI	p-ClC_6H_4-	C_6H_5-	125–126	Alcohol	80	—	—	[g]
XXXII	p-ClC_6H_4-	p-$CH_3C_6H_4$-	124–125	Alcohol	85	7.00	6.81	
XXXIII	$C_6H_5CH_2CH_2$	C_6H_5-	118–120	Alcohol	90	7.65	7.41	
XXXIV	C_6H_5-	p-$NO_2C_6H_4$	132–133	Alcohol	75	6.55	6.44	

[d] Reported m.p. 126–127° (dec.), Eibner.[12] [dd] Reported m.p. 128° (dec.).

[e] $C_{19}H_{18}N_2O_2S.{}^1/_2H_2O$:

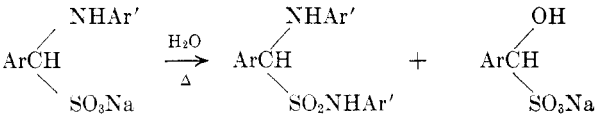
	C, %	H, %	N, %	S, %
Requires	65.51	5.47	8.07	9.22
Found[17]	65.38	5.40	7.95	9.11

[f] $C_{21}H_{22}N_2O_2S.{}^1/_2H_2O$:

Requires	67.14	6.173	7.463
Found[17]	66.38	6.258	7.18

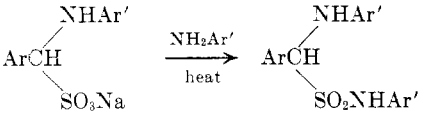
[g] $C_{19}H_{19}N_2O_2SCl$:

Requires	58.4	4.87	7.19
Found[17]	58.34	4.9	7.37

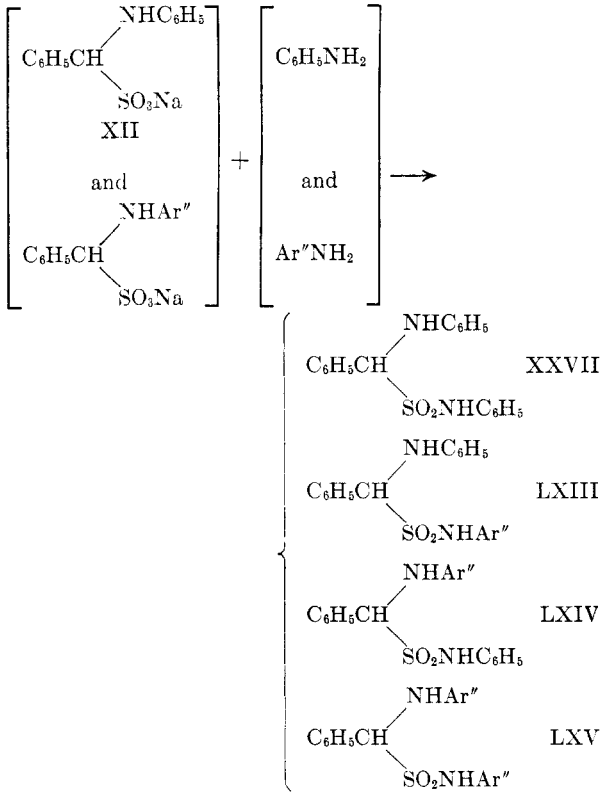


We have isolated both the amide and the aldehyde-bisulfite product. Sulfonamides of this type are known from the work of Eibner,[12] who prepared them by treating an aromatic aldehyde with an aromatic amine and sulfurous acid, or allowed the Schiff base to react in ether with sulfur dioxide. We were able to prepare such compounds in better yields by treating the desired aromatic aldehyde with two equivalents of sodium bisulfite followed by two equivalents of the aromatic amine, dissolving or suspending all in water, stirring and boiling for a few minutes; on cooling, the product crystallized in excellent yields. The compounds obtained in this manner are shown in Table II.

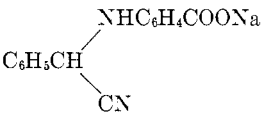
The compounds of Table II may also be obtained according to the reaction



However, when α-anilinophenylmethanesulfonate (XII) is heated with *p*-toluidine the product is not exclusively sulfotoluidide but rather a mixture. An identical mixture results when α-*p*-toluidinophenylmethanesulfonate (XIII) is heated with aniline. The products are quite as if one carried out the reaction simultaneously with four reagents as follows:



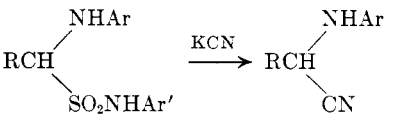
The separation of the mixture into its components by fractional crystallization or chromatography has not succeeded. However, by allowing XII to react with sodium *p*-aminobenzoate ($Ar''NH_2$ = *p*-$NH_2C_6H_4COONa$) a mixture was obtained where separation was more successful. The water insoluble product was identified as XXVII. The water-soluble portion was treated with potassium cyanide, as described below, replacing the sulfonamido group with the cyano group; an insoluble substance, identified as α-anilinophenylaceonitrile (IXL), was isolated, which had its origin in an intermediate of type LXIII. A soluble nitrile was also formed:



which may have its origin from types LXIV or LXV, but more probably from both, although this has not yet been unequivocally established.

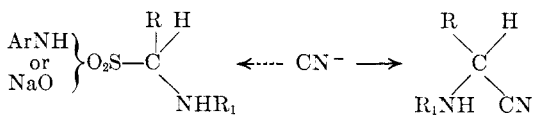
Further studies of these reactions are necessary before their machanism is understood. Since an amine-exchange is also possible, it cannot now be said that there is a reversion to aldehyde, amine, and bisulfite. The formation of sulfonanilides from sodium sulfonates in aqueous solution was unexpected.

The reaction of α-aminoalkanesulfonates with alkali cyanide to form nitriles has long been known.[13,14] We used it for the preparation of many α-amino nitriles, intermediate in the synthesis of amino acids not described here. Presumably this reaction also comes into play in the synthesis of α-hydroxylamino nitriles.[15] We find that the sulfonamide group is likewise susceptible to replacement by cyanide, giving identical nitriles, as listed in Table III.



The products may be obtained by stirring the reagents in water at room temperature, but their formation may be facilitated by employing alcohol solvent and heating for a short time.

If these reactions are considered as a base replacement and if formulated correctly to proceed as:



(12) A. von Eibner, *Ann.*, **316** 89 (1901).
(13) E. Knoevenagel, *Ber.*, **37**, 4073 (1904).
(14) W. V. Miller and J. Plöchl, *Ber.*, **25**, 2032 (1892).
(15) L. Neelakantan and W. H. Hartung, *J. Org. Chem.*, **23**, 964 (1958).

TABLE III

R—CH(NHAr)—CN

α-ARYLAMINONITRILES

No.	R—	Ar—	Crystals from	Yield, %	Melting Point Observed	Melting Point Reported	Remarks
XXXV	n-C_3H_7-	C_6H_5-	Pet. ether	75	50–51	51	[h]
XXXVI	i-C_3H_7-	C_6H_5-	Ether–pet. ether	70	54–55	54	[h]
XXXVII	n-C_4H_9-	C_6H_5-	Benzene–pet. ether	70	63–64	65	[h]
XXXVIII	i-C_4H_9-	C_6H_5-	Ether–pet. ether	68	67–68	67	[h]
IXL	C_6H_5-	C_6H_5-	Alcohol	90	85–86	85	[i]
XL	C_6H_5-	p-$CH_3C_6H_4$-	Alcohol	90	109–110	109–110	[i]
XLI	C_6H_5-	p-ClC_6H_4-	Alcohol	85	121–122	—	[j]
XLII	p-ClC_6H_4-	C_6H_5-	Alcohol	75	112–113	112	[k]
XLIII	p-ClC_6H_4-	p-$CH_3C_6H_4$-	Alcohol	70	81–82	80	[k]
XLIV	C_6H_5-	p-$C_6H_4CO_2H$	Alcohol	75	163–164	—	[l]
XLV	C_6H_5-	p-$NO_2C_6H_4$-	Alcohol	80	128–129	129	[m]
XLVI	$C_6H_4CH_2CH_2$	C_6H_5-	Ether	55	88–90	—	[n]

[h] W. V. Miller, *et al.*,[14] (1892). [i] E. Knoevenagel.[8] [j] $C_{14}H_{11}N_2Cl$ requires N, 11.6. Found N, 11.45. [k] Walther, *et al.*, *J. pr. chem.* (2) **65**, 269. [l] $C_{15}H_{12}N_2O_2$ requires N, 11.1. Found N, 11.34. [m] H. Rohde, *et al.*, *Ber.*, **25**, 2054 (1892). [n] $C_{16}H_{15}N_2$ requires N, 11.9. Found N, 11.75.

TABLE IV

R—CH(NHAr)—CH(COOEt)(COOEt)

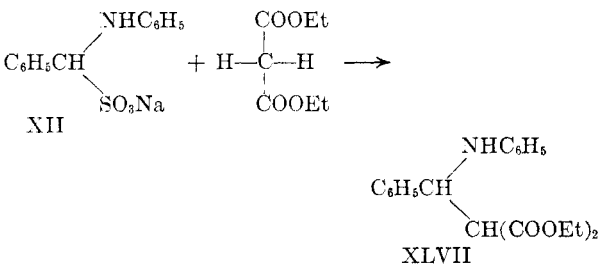
β-ARYL-β-ARYLAMINO-METHYL MALONIC ESTERS

No.	R—	Ar—	Crystals from	Yield, %	Melting Point Observed	Melting Point Reported	Procedure	Remarks
XLVII	C_6H_5-	C_6H_5-	Benzene-ligroin	85 75	99–100	100–101	A B	[o]
XLVII	C_6H_5-	p-$CH_3C_6H_4$	Alcohol	70 50	82–83	80–82	A B	[o]
XLIX	C_6H_5-	p-ClC_6H_4-	Alcohol	60 55	81–82	81–82	A B	[o]
L	C_6H_5-	p-$C_6H_4CO_2H$	Alcohol	75	164–165	164–165	A	[o]
LI	p-ClC_6H_4	C_6H_5-	Alcohol	70 55	119–120	—	A B	[p]
LII	p-ClC_6H_4	p-$CH_3C_6H_4$-	Alcohol	65 50	106–107	—	A B	[q]

[o] E. J. Wayne and J. B. Cohen, *J. Chem. Soc.*, 127, 450 (1925).

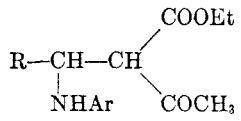
		C	H	N
[p] $C_{20}H_{22}NO_4Cl$:	Requires	63.9	5.9	3.72
	Found	64.1	6.1	3.65[17]
[q] $C_{21}H_{24}NO_4Cl$:	Requires	N, 3.63		
	Found	N, 3.5		

then other bases may be expected to react in an analogous manner, if proper conditions are employed, and a typical equation may be assumed with diethyl malonate to become:



We found this reaction to proceed very well if catalytic amounts of base are employed, *e.g.*, small amounts of sodium ethoxide, piperidine, diethylamine, benzylamine, or even sodium hydroxide. The reaction may be carried out in alcohol simply by mixing the reagents as a suspension, if insoluble, or in water and stirring at room temperature for three days as necessary, when excellent yields of product are formed. Ethyl acetoacetate and acetylacetone are alkylated with equal readiness, in some instances even without the presence of the catalytic base. The products prepared by these reactions are listed in Tables IV, V, and VI. It will be noted

TABLE V



β-ARYL-β-ARYLAMINO-METHYL ACETOACETIC ESTERS

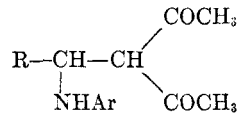
No.	R—	Ar—	Crystals from	Procedure	Yield, %	Melting Point Observed	Melting Point Reported	Remarks
LIII	C_6H_5-	C_6H_5-	Ligroin	A	85	106–107	107–108	[r]
				B	65			
LIV	C_6H_5-	p-$CH_3C_6H_4$-	Benzene–pet. ether	A	80	96–97	97	[r]
				B	55			
LV	C_6H_5-	p-ClC_6H_4-	Alcohol	A	85	112–113	112	[r]
				B	65			
LVI	p-ClC_6H_4	C_6H_5-	Alcohol	A	80	116–117	—	
				B	70			
LVII	p-ClC_6H_4-	p-$CH_3C_6H_4$	Benzene–pet. ether	A	65	112–113	—	[t]

[r] Siegfried Rohemann, *J. Chem. Soc.*, 85, 1177, 1452 (1904).

		C, %	H, %	N, %
[s] $C_{19}H_{20}NO_3Cl$:	Requires	66.07	5.797	4.057
	Found	65.87	5.78	3.95[17]

[t] $C_{20}H_{22}NO_3Cl$: Requires: N, 3.91. Found: N, 4.12.

TABLE VI



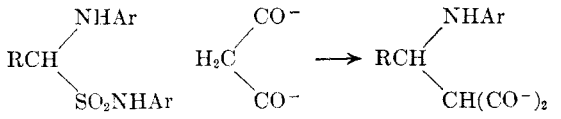
β-ARYL-β-ARYLAMINOMETHYL ACETYLACETONES

No.	R—	Ar—	Crystals from	Procedure	Yield, %	Melting Point Observed	Melting Point Reported	Remarks
LVIII	C_6H_5-	C_6H_5-	Alcohol	A	65	112–113	113	[u]
				B	50			
LIX	C_6H_5-	p-$CH_3C_6H_4$-	Alcohol	A	75	96–97	96	[u]
LX	C_6H_5-	p-ClC_6H_4-	Alcohol	A	70	99–100	99	[u]
LXI	p-ClC_6H_4-	C_6H_5-	Alcohol	A	75	118–119	—	[v]
				B	55			
LXII	p-ClC_6H_4-	p-$CH_3C_6H_4$-	Alcohol	A	55	106–107	—	[w]

[u] S. Ruhemann and E. R. Watson, *J. Chem. Soc.*, 85, 466 (1904). [v] $C_{17}H_{17}NO_2Cl$ requires N, 4.43, found N, 4.48 [w] $C_{18}H_{19}NO_2Cl$ requires N, 4.3, found N, 4.15.

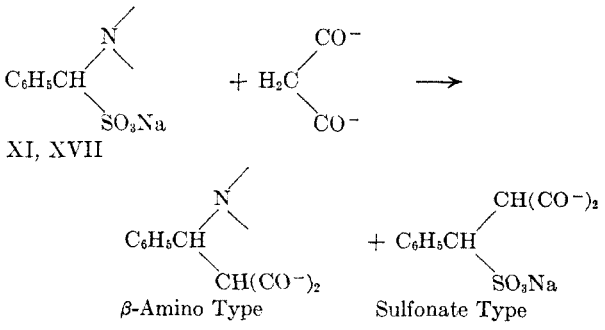
that some of these compounds have been prepared by previous investigators employing other procedures. We have not yet examined these products to determine whether they behave in the manner characteristic for β-amino ketones or β-amino esters.

We have further observed that the alkylation proceeds also with sulfonamides, affording products identical with those obtained *via* the sulfonates. Also only catalytic amounts of base are required to promote the reaction with:



active methylene reagents.

When the amino group of the sulfonate is unsubstituted or bears a nonaromatic substituent, it reacts with diethyl malonate in two directions, *e.g.*:



XI, XVII

β-Amino Type Sulfonate Type

The primary amino sulfonate reacts with diethyl malonate to form 5 to 10% β-amino type and 60% sulfonate type; but with ethyl acetoacetate only product of sulfonate type was isolated. A compound

of this type is known from the work of Raschig[16] who allowed ethyl acetoacetate to react with formaldehyde - bisulfite in the presence of sodium hydroxide. The piperidino sulfonate (XVII) reacts with ethyl acetoacetate as does the primary amino sulfonate; and ethyl cyanoacetate reacts as does ethyl acetoacetate.

The mechanism of these alkylation reactions is not yet clear. It is hoped that studies now under way will shed more light on the pathway by which these products are formed.

EXPERIMENTAL

The laboratory procedures employed for synthesizing the various compounds are adaptations and improvements on published directions. Below are given typical examples. By appropriate selection of reagents a large number of compounds become possible. The pertinent data for the present series are summarized in the respective Tables.

Sodium α-anilinophenylmethanesulfonate (XII). One-tenth mol. of benzaldehyde, 10.6 g., was stirred with a solution of 0.1 mol. of bisulfite, 10.5 g., in 50 ml. of water for 1 hr., after which 0.1 mol. aniline, 9.3 g., was added; the mixture was stirred and carefully warmed on a water bath, forming in a few minutes a clear solution; this was cooled and yielded a crystalline product, which was collected on a Buchner funnel, washed with cold water, dried, and recrystallized from alcohol.

One-tenth mol. of benzylidineaniline, 18.1 g., was warmed in a solution of 0.14 mol. sodium bisulfite, 15 g., in 100 ml. water to 60°, and after about an hour a clear solution resulted. On cooling, a colorless crystalline product was obtained, which was washed with cold water, dried, and recrystallized from alcohol.

α-Anilinophenylmethanesulfonanilide (XXVII). One-tenth mol. benzaldehyde, 10.6 g., was stirred for an hour with a solution of 0.2 mol. sodium bisulfite, 20.8 g., in 100 ml. of water, after which 0.2 mol. aniline, 18.6 g., was added; the mixture was stirred and heated on a water bath for 15 min. and then boiled for 10 min.; on standing, the solution formed colorless slender needles, which may be recrystallized from hot water or from ethanol.

α-Aminophenylacetonitrile. One-tenth mol. of sodium α-aminophenylmethanesulfonate (XI), 20.9 g., in 50 ml. of water treated with a solution of 0.1 mol. sodium cyanide, 5.0 g., in a small amount of water and stirred for about 5 min. at room temperature; an oil separated, which, on standing at 0° for 2 hr. solidified. The product was collected, washed with cold water, dried, and recrystallized from ligroin.

(16) F. v. Raschig and W. Prahl, *Ann.*, **448**, 265 (1926).

α-Anilinophenylacetonitrile (IXL). One-tenth mol. of sodium α-anilinophenylmethanesulfonate (XII), 28.5 g., and 0.1 mol. potassium cyanide, 6.5 g., were heated to reflux in 100 ml. alcohol for 1 hr. The mixture was then cooled, inorganic salt filtered off, and the filtrate concentrated under reduced pressure to about 40 ml. On cooling, a crystalline mass formed, which was recrystallized from alcohol, yielding colorless crystals.

One-twentieth mol. of α-anilinophenylmethanesulfonanilide (XXVII), 17.5 g., and 0.05 mol. potassium cyanide, 3.3 g., were refluxed in 60 ml. of alcohol for 1 hr.; the solution was then concentrated to about 35 ml. under reduced pressure; on cooling a crystalline product formed, which was purified as described above.

α-Aminoalkanesulfonates and derivatives with active methylene compounds. Procedure A. One-tenth mol. of sodium α-anilinophenylmethanesulfonate (XII), 20.9 g., 0.1 mol. diethyl malonate, 16 g., and 2 drops of piperidine was stirred for 3 days in 100 ml. water at room temperature. An oily solid formed; this was extracted with benzene, the benzene volatilized in a current of air, and a crystalline solid remained; this was crystallized from ethanol. The reaction may be expedited by refluxing rather than allowing it to proceed at room temperature. Ethyl acetoacetate or acetylacetone may be employed instead of diethyl malonate with equally favorable alkylation yields.

Procedure B. One-tenth mol. of α-anilinophenylmethanesulfonanilide (XXVII), 35.0 g., 0.1 mol. diethyl malonate, 16 g., 2 drops of piperidine, and 150 ml. of alcohol were heated to reflux for about 1 hr.; the solution was then concentrated by a current of air to about half its volume and poured into 300 ml. of ice water; after a day the crystalline product was removed, dried, washed with petroleum ether, and recrystallized from alcohol. The reagents may also be suspended or dissolved in water, stirred for 3 days at room temperature, and the products isolated and purified in the usual manner.

Procedure C. One-tenth mol. of sodium α-aminophenylmethanesulfonate (XI), 20.9 g., in 60 ml. of water was treated with 0.1 mol. of ethyl acetoacetate, 13 g., and 2 drops of piperidine. After stirring for 15 min. it formed a clear solution, but stirring was continued for a day and then placed in the refrigerator for 12 hr., whereupon a colorless crystalline substance formed; this was collected on a Buchner funnel, washed with a little water and then cold alcohol, and then recrystallized from alcohol, giving 29 g., 90%, of pure product, m.p. 182–183° (dec.), which was identified as sodium 1-phenyl-2-acetyl-2-carbethoxyethane-1-sulfonate.

Anal. Calcd. for $C_{13}H_{15}O_6SNa.H_2O$: C, 45.87; H, 5.0. Found:[17] C, 45.45; H, 5.4.

The test for presence of nitrogen was negative.

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(17) Analyses by Messrs. Weiler and Strauss, Oxford, England.