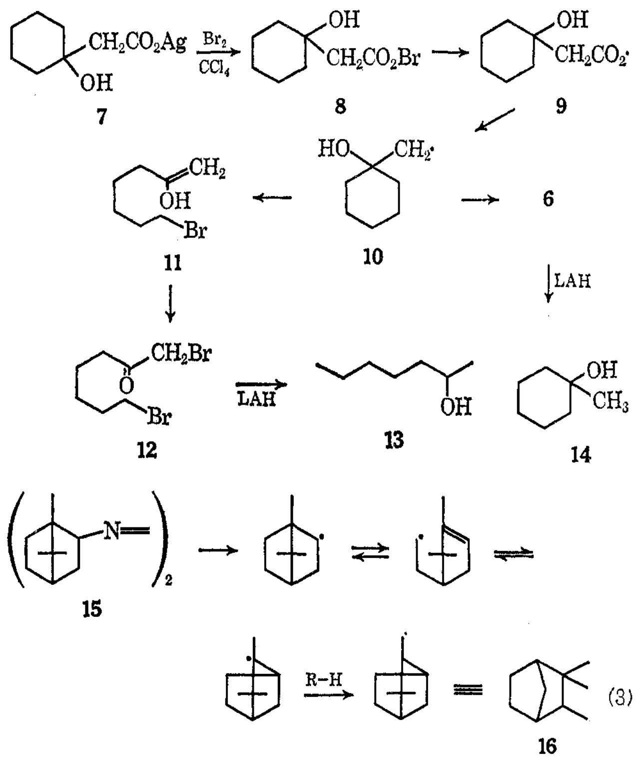
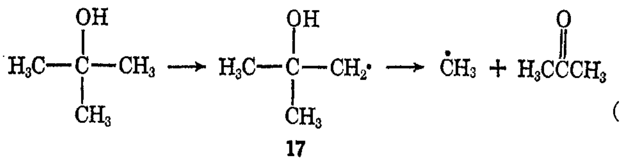
SCHEME I

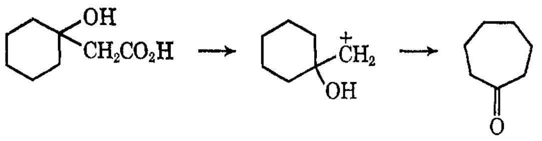




$$H_3C-\underset{CH_3}{\overset{OH}{C}}-CH_3 \longrightarrow H_3C-\underset{CH_3}{\overset{OH}{C}}-CH_2\cdot \longrightarrow \dot{C}H_3 + H_3C\overset{O}{\overset{\|}{C}}CH_3 \qquad (4)$$

17

The free-radical nature of the Hunsdiecker reaction is well established[9] although ionic pathways have also been postulated.[10] The formation of mainly open-chain products described herein *via* ring cleavage strongly points to the presence of free radicals. It has been shown[11] that a carbonium ion generated from 1-hydroxycyclohexylacetic acid by electrolysis affords cycloheptanone in 45–53% yield (eq 5). The Hunsdiecker reaction with other β-hydroxy acids is presently under investigation.



(5)

Experimental Section[12]

1-Hydroxycyclohexylacetic acid, mp 64–66° (lit.[13] mp 62–64°), was quantitatively converted into the silver salt in the usual manner.[14] To a stirred solution of 8 g (0.05 mol) of bromine in carbon tetrachloride (50 ml) at 60–65° was added 14 g (0.052 mol) of the dried powdered silver salt in portions. Carbon dioxide evolution occurred during the 10-min addition period. The mixture was then refluxed for 30 min, cooled, and filtered. The carbon tetrachloride solution, after dilution with ether, was washed with a sodium bicarbonate solution to remove a considerable amount of the reformed starting acid, 5.8 g (0.037 mol). The carbon tetrachloride was dried (magnesium sulfate) and the solvent removed under vacuum. A yellow liquid residue remained (5 g) which showed infrared absorptions at ν_{CCl_4} 1780, 1740 and 1700 cm^{-1}.

To a stirred refluxing suspension of lithium aluminum hydride (2 g) in dry ether (40 ml) a solution of the crude bromo ketone (5.0 g) in ether (40 ml) was added dropwise. The mixture was stirred and refluxed for 15 hr. It was then cooled and decomposed with saturated sodium sulfate solution. The ether layer was separated and the remaining solid was washed with ether. The combined ether extracts were dried over magnesium sulfate and the solvent removed. The residue upon distillation afforded a fraction of bp 73–75° (20 mm). There was isolated 0.5 g (0.0043 mol) (30% of the recovered acid was taken into account). Vpc analysis on a 4-ft TCEP column and a 4-ft Carbowax column at 100° (40 psi) revealed it to be a mixture of 2-heptanol (90%) and 1-methylcyclohexanol (10%). The infrared and nmr spectra were identical with those of authentic 2-heptanol. The 3,5-dinitrobenzoate was also found to be identical with that of authentic 2-heptanol (melting point and mixture melting point).

The silver salt of 1-hydroxycyclopentylacetic acid[13] under similar conditions (Hunsdiecker followed by lithium aluminum hydride reduction) afforded a liquid, bp 135–136° (15%). This was found to be exclusively 2-hexanol from the infrared and nmr spectra as well as vpc analysis. Comparison of the 3,5-dinitrobenzoates also confirmed the structural assignment.

Registry No.—1-Hydroxycyclopentylacetic acid (Ag salt), 18500-78-2; 7, 18500-79-3.

Acknowledgment.—We are grateful to Mr. T. Kolesar for taking the nmr spectra.

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[8] M. S. Kharasch, J. Rowe, and W. H. Urry, *J. Org. Chem.*, **16**, 905 (1951).

[9] C. V. Wilson, *Org. Reactions*, **9**, 332 (1957); R. G. Johnson and R. K. Ingham, *Chem. Rev.*, **56**, 219 (1956).

[10] U. K. Pandit and I. P. Dirk, *Tetrahedron Lett.*, No. 14, 891 (1963); H. W. Blunt, University Microfilms, Ann Arbor, Mich., Order No. 66-4602; *Dissertation Abstr.*, **26** (12), 7030 (1966).

[11] E. J. Corey, N. L. Bauld, R. T. Lalonde, J. Cassanova, Jr., and E. T. Kaiser, *J. Amer. Chem. Soc.*, **82**, 2645 (1960).

[12] All melting points and boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Spectrocord infrared spectrophotometer. Nmr spectra were determined with a Varian A-60 instrument.

[13] J. Maillard, M. Benard, and R. Morin, *Bull. Soc. Chim. Fr.*, 244 (1958).

[14] E. W. Warnhoff, C. M. Wong, and W. T. Tai, *J. Org. Chem.*, **32**, 2664 (1967).

N-Alkylanilinomethylenemalononitriles. A Convenient Synthesis through a Variation and Extension of the Meerwein Amide Acetal Reaction

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Received June 27, 1968

Amide acetals are readily prepared by reaction of tertiary amides with triethyloxonium tetrafluoroborate,[1] followed by addition of base and alcohol.[2] Meerwein and coworkers[2] have demonstrated the great synthetic utility of amide acetals. One example is the reaction of N,N-dialkylamide acetals with malononitrile to form N,N-dialkylaminomethylenemalononitriles.[2] Desirous of an easy route to N,N-disubstituted aminomethylenemalononitriles, we have explored a variation of this synthetic route and have extended this reaction to a convenient synthesis of N-alkylanilinomethylenemalononitriles.

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[1] Triethyloxonium tetrafluoroborate is quite easily prepared from boron trifluoride etherate and epichlorohydrin: H. Meerwein, *Org. Syn.*, **46**, 113 (1966).

[2] H. Meerwein, W. Florian, N. Schön, and G. Stopp, *Ann* **641**, 1 (1961).

Reaction of N-alkylformanilides with triethyloxonium tetrafluoroborate in methylene chloride at 20–25° generally is complete within 1–3 hr with formation of ethoxymethylene-N-alkyl-N-arylammonium tetrafluoroborates.[3] These ammonium tetrafluoroborates, without isolation, can be condensed with malononitrile employing triethylamine as a catalyst. The preparation of **1**–**5** indicates that the reaction is quite general in scope (Scheme I, Table I).

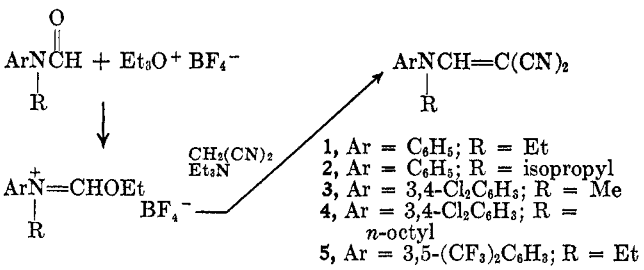
TABLE I

N-ALKYLANILINOMETHYLENEMALONONITRILES

Compd	Mp, °C	% yield	Crystn solvent	Calcd, %			Found, %		
				C	H	N	C	H	N
1	70–72	58	Aq MeOH[a]	73.07	5.62		73.14	5.53	
2	139–140	54	EtOH	73.91	6.20	19.89	73.71	6.09	19.68
3	163–164	54	MeOH	52.41	2.80	16.68	52.22	2.73	16.58
4	Oil	27[b]		61.72	6.04	12.00	61.94	6.22	11.84
5	118–120	54	Aq MeOH	50.46	2.72		50.59	2.78	

[a] Rapidly chromatographed on neutral activity I alumina with benzene and then crystallized. [b] The purification by chromatography was interrupted for a weekend after some pure product (27%) was eluted. The residual product on the column decomposed.

SCHEME I



Experimental Section

Melting points were taken in open capillary tubes with a Mel-Temp apparatus and are corrected. Ir spectra were determined with a Beckman IR-5 spectrometer. Some of the starting formanilides are new; their preparations are given below.

3′,4′-Dichloro-N-methylformanilide.—The method of Roberts and Vogt[4] for preparation of N-methylformanilides was employed. From reaction of 3,4-dichloroaniline and trimethyl orthoformate was obtained, after two distillations, pure product in 40% yield: bp 153° (5 mm); mp 37.5–38.5°; ir ($CHCl_3$) 1675 cm^{-1} (C=O).

Anal. Calcd for $C_8H_7Cl_2NO$: C, 47.09; H, 3.46. Found: C, 46.98; H, 3.43.

3′,4′-Dichloro-N-octylformanilide.—A solution of 82.2 g (0.30 mol) of 3,4-dichloro-N-octylaniline (prepared and generously supplied by Dr. J. Olin of these laboratories) and 100 g (2.18 mol, 97+%) of formic acid was held 24 hr at reflux. Distillation of the reaction mixture gave 78.2 g (86%) of product: bp 155° (0.25 mm); $n^{23}{}_D$ 1.5374; ir (liquid film) 1670 cm^{-1} (C=O).

Anal. Calcd for $C_{15}H_{21}Cl_2NO$: C, 59.60; H, 7.00. Found: C, 59.78; H, 6.89.

N-Ethyl-α,α,α,α′,α′,α′-hexafluoro-3,5-formoxylidide.—The method of Roberts and Vogt[4] for preparation of N-ethylformanilides was employed. The product from reaction of α,α,α,α′,α′,α′-hexafluoro-3,5-xylidine and triethyl orthoformate was distilled twice to give pure product in 33% yield: bp 134–135° (20 mm); ir (CCl_4) 1690 cm^{-1} (C=O).

Anal. Calcd for $C_{11}H_9F_6NO$: C, 46.33; H, 3.18. Found: C, 46.43; H, 3.38.

General Procedure for Anilinomethylenemalononitriles.—The N-alkylformanilide (0.10 mol) in 40 ml of methylene chloride is added to a solution of triethyloxonium tetrafluoroborate (0.11 mol) in 60 ml of methylene chloride. The resultant solution is allowed to stand 1.5–3 hr, and then malononitrile (0.12 mol) is added. Triethylamine (0.13 mol) is added dropwise with stirring and cooling in an ice bath. The solution is then stirred overnight at room temperature. Methylene chloride (300 ml) is added, and the solution is extracted with three 100-ml portions of water. The organic layer is dried (Na_2SO_4) and concentrated under vacuum. The crude product is purified by crystallization from an appropriate solvent or by *rapid* chromatography on neutral activity I alumina with benzene.

In general, the ir spectra (Nujol mull or $CHCl_3$) of the N-alkylanilinomethylenemalononitriles displayed CN absorption at 2200–2220 cm^{-1} and C=C absorptions at 1615–1620, 1585–1595, and 1470–1490 cm^{-1}.

Registry No.—**1**, 18153-45-2; **2**, 18153-46-3; **3**, 18153-47-4; **4**, 18153-48-5; **5**, 18181-26-5; 3′,4′-dichloro-N-methylformanilide, 18153-49-6; 3′,4′-dichloro-N-octylformanilide, 18153-50-9; N-ethyl-α,α,α,α′,α′,α′-hexafluoro-3,5-formoxylidide, 18153-51-0.

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(3) The reaction is conveniently monitored by nmr by observing the disappearance of triethyloxonium tetrafluoroborate.

(4) R. M. Roberts and P. J. Vogt, *J. Amer. Chem. Soc.*, **78**, 4778 (1956).

The Thermal Rearrangement of α-Phenylazo-β-benzoyloxystilbene. II. The Effect of Substituents on Rate

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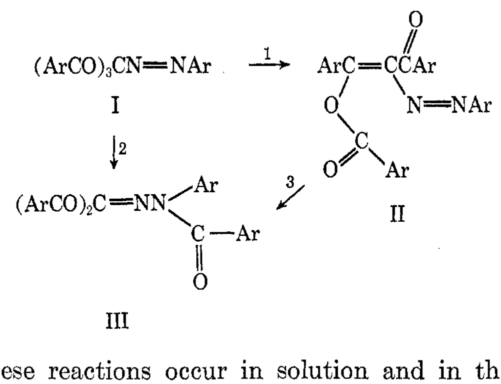
Received June 28, 1968

Curtin and coworkers[1] have studied the rearrangement of arylazotriaroylmethanes (I) to the corresponding enol esters (II) and aroylhydrazones (III) (Scheme I).

SCHEME I



These reactions occur in solution and in the solid state. These workers found all three reactions in

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(1) (a) D. Y. Curtin and M. L. Poutsma, *J. Amer. Chem. Soc.*, **84**, 4887, 4892 (1962); (b) R. T. Puckett, C. E. Pfluger, and D. Y. Curtin, *ibid.*, **88**, 4637 (1966); (c) D. Y. Curtin and L. L. Miller, *ibid.*, **89**, 637 (1967).