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).

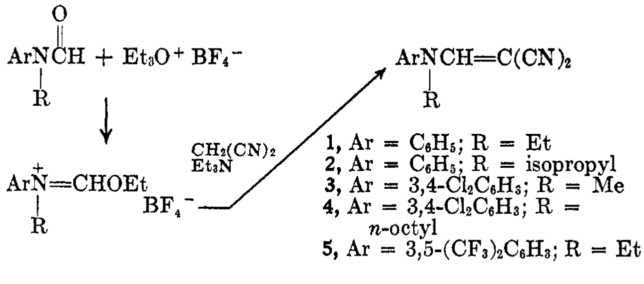
TABLE I

N-ALKYLANILINOMETHYLENEMALONONITRILES

Compd	Mp, °C	% yield	Crystn solvent	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % 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$_8$H$_7$Cl$_2$NO: 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$_2$NO: 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$_9$F$_6$NO: 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$_2$SO$_4$) 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.

---

[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

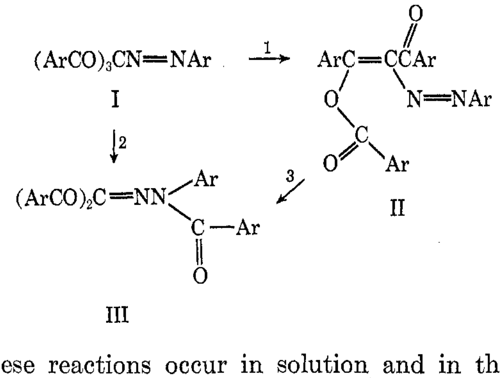
C. S. RUSSELL, KENNETH STROTHKAMP, AND DUKE KASPRISIN

Department of Chemistry,
The City College of the City University of New York,
New York, New York 10031

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

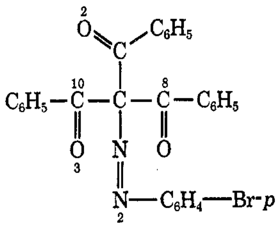


These reactions occur in solution and in the solid state. These workers found all three reactions in

---

[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).

solution to be first order, and to be retarded by a *p*-methoxy group and accelerated by *p*-nitro and 2,4,6-trichloro substituents in the phenylazo moiety. Reactions 1 and 2 proceed at comparable rates but reaction 3 is about 55 times slower. Single crystal X-ray studies of Ia[1b] provide interatomic distances

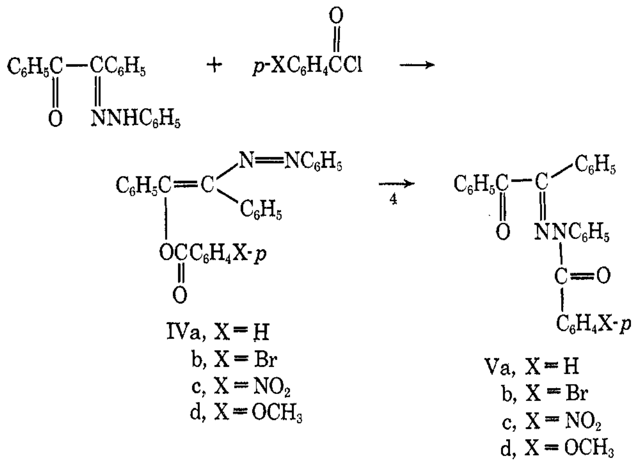


Ia

which indicate that the reaction is probably intramolecular in the solid state. The results also suggest to us that spatially, rearrangement of aroyl from C to O to give the *cis* or *trans* enol benzoate is equally favored. That is, the C-10 to O-2 and C-8 to O-3 distances are both 2.69 Å. It is plausible to suppose as Curtin did[1b] that both isomers are formed but that the *cis* isomer rearranges rapidly to III and that II is only *trans*.

We have studied a simpler model of reaction 3.[2] Aroylation of benzil phenylhydrazone in pyridine yields the enol ester IV which rearranges in solution or in the solid state to the aroylhydrazone V (Scheme II).

Scheme II



In order to probe reaction 4 further, we have studied the effect of *para* substituents in the migrating group on the rate of rearrangement. To this end, IVa–d were prepared and the kinetics of rearrangement in decalin were studied. The data are presented in Table I.

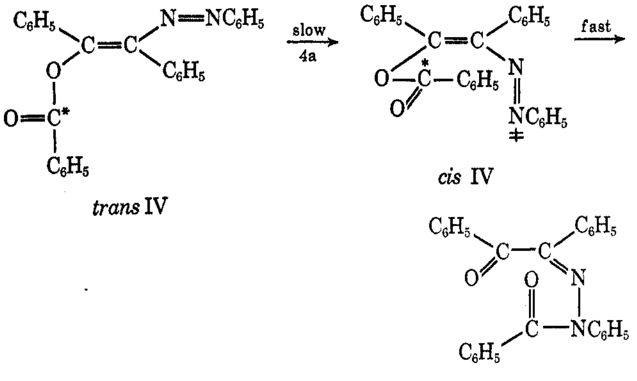
The kinetics were first order. In the case of IVa, we found no dramatic solvent effect in going from ethylene glycol monomethyl ether to decalin. We also found no dramatic substituent effect although *para* substituents were chosen for their marked ability to produce such effects in other reactions. The *p*-nitro group shows a mild accelerating effect. Complete spectra of all the samples in the kinetic runs showed only starting material and product.

Table I

The Effect of Substituents on the First-Order Rate Constants for the Rearrangement of α-Phenylazo-β-(*p*-X-benzoyloxy)stilbene (IV)

X	Solvent	*T*, °C (±0.2°)	$k \times 10^5$ (± mean error)
H	$HOCH_2CH_2OCH_3$, decalin	101.5	11.1 ± 0.2
		101.9	10.3 ± 0.1
		101.8	9.11 ± 0.03
		102.0	9.44 ± 0.10
		111.9	24.5 ± 1.3
		111.9	24.1 ± 0.4
Br	Decalin	102.0	9.36 ± 0.19
		102.0	9.55 ± 0.03
		112.0	22.6 ± 0.2
		112.0	22.1 ± 0.2
NO_2	Decalin	102.0	10.4 ± 0.2
		102.0	10.4 ± 0.2
		101.8	10.1 ± 0.1
		111.8	25.6 ± 1.1
		111.8	26.0 ± 0.4
OCH_3	Decalin	102.0	9.16 ± 0.21
		102.0	9.32 ± 0.09
		111.9	24.7 ± 0.3
		111.9	24.1 ± 0.3

These results suggest that reaction 4 occurs in two steps. If enol ester IV is assigned the *trans* structure, then isomerization to or toward the *cis* isomer would then be the rate-determining step and migration of the aroyl group a fast second step. This mechanism accounts for the insensitivity in the rate to *para* substituents in the migrating group.



It is not essential to implicate the *cis* isomer as an intermediate. One can visualize a singlet state[3] in which rotation of 90° from the plane of the *trans* isomer is the barrier which must be overcome to place the carbonyl carbon (*) within bonding distance of the azo nitrogen (≠). The small accelerating effect of the nitro group might be the result of such a transition.

Another explanation of these results is that IV is the *cis* isomer. Then only a cyclic intermediate (step 4b) need be considered, in which charge separation is so small that the rate is almost insensitive to substituents. This last is an unattractive alternative because Curtin[1a] found a pronounced substituent effect for their analogous enol benzoate to hydrazone rearrangement (reaction 3) when substituents were placed in the phenylazo moiety. The rate of *p*-nitro compound II was 12 times as fast as for unsubstituted II. This result is not unexpected in the first postulated isomerization mechanism; substituents could have a profound

---

(2) C. S. Russell and D. Weisleder, *J. Org. Chem.*, **32**, 2626 (1967).

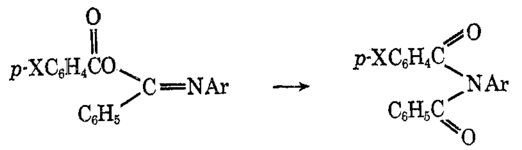
(3) M. C. Lin and K. J. Laidler, *Can. J. Chem.*, **46**, 973 (1968).

TABLE II

Compd no.	Substituent	Formula	Mp,[a] °C	Ir maxima in carbonyl region, cm^{-1}	Uv and visible maxima, mμ (ε)	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
IVb	Br	$C_{27}H_{19}O_2N_2Br$	148.5–149[b]	1740	251 (4.14×10^4) 346–350 (2.31×10^4) 450–458 (4.83×10^2)	67.09	3.96		67.25	4.11	
Vb	Br		177–179	1675 1660 (sh)	251–255 (2.66×10^4)	67.09	3.96		66.84	3.93	
IVc	NO_2	$C_{27}H_{19}O_4N_3$	164–165[b]	1755	255 (3.08×10^4) 343–351 (1.98×10^4) 450 (4.76×10^2)	72.15	4.26	9.35	72.22	4.32	9.59
Vc	NO_2		167.5–168	1690 (sh) 1670	257–260 (3.02×10^4)	72.15	4.26	9.35	72.91	4.28	9.33
IVd	OCH_3	$C_{28}H_{22}O_3N_2$	143–146[b]	1740	259–260 (2.70×10^4) 347–352 (2.01×10^4) 446–458 (4.96×10^2)	77.40	5.14	6.46	77.08	5.02	
Vd	OCH_3		163–164	1680 1670 (sh)	255–257 (2.80×10^4)	77.40	5.14	6.46	76.87	5.07	6.56

[a] Melting points of the azo esters were obtained by placing a sample into the Mel-Temp apparatus at about 120° and heating at 2 deg/min. [b] These compounds crystallize as red nuggets and yellow needles. The yellow needles showed a fuzzier melting point. However, both kinds of crystals melted to a red melt which decolorized to the rearranged product. Both kinds of crystals move as one spot on Chromagram sheet. Their infrared spectra appeared identical.

effect on the stability of the singlet whose formation is rate determining.[3] The isomerization mechanism is also strengthened and the single step postulate weakened by the finding of a marked substituent effect in the benzimidoyl benzoate rearrangement[1c] where aroyl migration is rate determining. Work with enol benzoates (IV) in which substituents are placed on the stilbene phenyl groups is in progress. Preliminary work suggests that p-nitro substituents on the stilbene phenyl groups have a retarding effect on the rate of reaction 4.



The rearrangement is particularly intriguing in the solid state. It can be followed under the microscope by changes in color from the red enol benzoate (IV) to the colorless hydrazone V. V forms whiskers on the surface of the crystal and at defect points. The red crystal becomes opaque but retains its shape. V sublimes appreciably at about 105° for the several days which the solid state rearrangement requires. This escape of some of the product from the crystal undoubtedly produces many holes which act as new defects to initiate reaction. A "shrinking" in the crystal at the reaction locus would provide enough space for rotation and reorientation of groups in the molecule. A sample of IVb is in the hands of an X-ray crystallographer for further study.

Experimental Section

Microanalyses were performed by Schwarzkopf Microanalytical Laboratory. Infrared spectra were measured in a Perkin-Elmer Model 137 spectrophotometer and ultraviolet spectra in a Beckman DU spectrophotometer and in a Perkin-Elmer Model 202 spectrophotometer.

Rates of Rearrangement of α-Phenylazo-β-(p-X-benzoyloxy)-stilbenes (IV).—The rates of rearrangement in decalin were studied at two temperatures by following changes in absorption at 350 mμ as previously described.[2] The expression for first-order constants was

$$\ln \frac{OD_0^{350} - C_0(\epsilon_V^{350})}{OD_t^{350} - C_0(\epsilon_V^{350})}/t$$

where OD_0^{350} is optical density at 350 mμ at 0 time, OD_t^{350} is optical density at 350 mμ at time t, C_0 is concentration of IV at time 0, and ϵ_V^{350} is the extinction coefficient of V at 350 mμ.

α-Phenylazo-β-(p-X-benzoyloxy)stilbenes (IV) were prepared as described previously[2] for IVa. They could be purified on Eastman chromatogram sheet as previously described,[2] or by column chromatography on Florisil packed in hexane with benzene as eluent. The properties of these compounds and their rearranged products are described in Table II.

Registry No.—IVb, 18153-62-3; IVc, 18153-63-4; IVd, 18153-64-5; Vb, 18181-27-6; Vc, 18153-65-6; Vd, 18153-66-7.

Acknowledgment.—This work was supported in part by a Faculty Research Grant from the City University of New York.

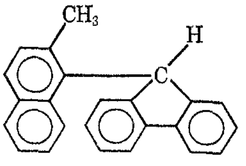
Proton Magnetic Resonance Studies of Slow Rotation in 9-Arylfluorenes[1]

T. H. SIDDALL, III AND W. E. STEWART

E. I. du Pont de Nemours and Company,
Aiken, South Carolina 29801

Received July 1, 1968

Slow rotation around the bond between the aryl group and the central carbon atom is reported for five 9-arylfluorenes. Kinetic quantities were determined for two of these by pmr signal shape analysis. One was isolated as one isomer in greater than 90% isomer purity. The barrier to rotation in this compound (E_a) is 29.8 kcal/mol.



---

[1] The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.