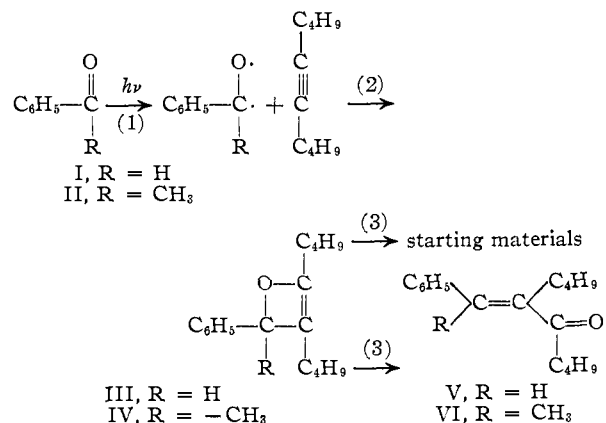


comparison of the 2,4-DNP's as well as infrared comparison of the homogeneous saturated ketones (VII).

A 1:1 mixture of acetophenone and 5-decyne was irradiated for 84 hours and the reaction product, 2-phenyl-3-*n*-butyl-2-octene-4-one (VI), isolated by distillation followed by chromatography of the fraction b.p. 110–125° (0.35 mm.). The structural assignment for VI rests on the following data: (1) b.p. 120–125° (0.35 mm.); infrared max. 5.95 μ ; λ_{\max} 248 $m\mu$ ($\log \epsilon$ 3.77); (2) catalytic reduction of VI over Pd/CaCO₃ catalyst resulted in the formation of VIII (C₁₈H₂₈O), infrared max. 5.85 μ ; (3) reduction of VI with sodium borohydride gave the corresponding unsaturated alcohol IX characterized by its 3,5-dinitrobenzoate m.p. 109–110° (*Anal.* Calcd. for C₂₅H₃₀N₂O₆: C, 66.06; H, 6.65. Found: C, 66.27; H, 6.54) and (4) synthesis of VI by an unambiguous route. Reformatsky condensation of ethyl α -bromocaproate with acetophenone gave X, infrared max. 2.95, 5.88 μ (*Anal.* Calcd. for C₁₆H₂₄O₂: C, 72.69; H, 9.15. Found: C, 72.83; H, 9.28) which was converted to the unsaturated ester XI, (infrared max. 5.82 μ ; λ_{\max} 237 $m\mu$ ($\log \epsilon$ 3.95); *anal.* Calcd. for C₁₆H₂₂O₂: C, 78.01; H, 9.00. Found: C, 78.13; H, 9.09) by dehydration with iodine. α -*n*-Butyl- β -methylcinnamic acid (XII) obtained by base hydrolysis of XI (characterized by its amide m.p. 164–164.5°, *anal.* Calcd. for C₁₄H₁₉NO: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.27; H, 8.67; N, 6.38; λ_{\max} 229 $m\mu$ ($\log \epsilon$ 3.95)) was converted to the acid chloride and condensed with dibutylcadmium to give (VI), b.p. 112–114° (0.15 mm.); infrared max. 5.95 μ ; λ_{\max} 245 $m\mu$ ($\log \epsilon$ 3.83); *anal.* Calcd. for C₁₈H₂₆O: C, 83.66; H, 10.14. Found: C, 83.93; H, 9.95. Identity with the product (VI) described above was established by spectral comparison and mixed m.p. determination of the 3,5-dinitrobenzoate of the corresponding secondary alcohol. The unsaturated ketones (V and VI) produced in the photochemical process appear to be a mixture of *cis* and *trans* isomers but we have so far been unable to achieve complete separation. The fact that the infrared spectra of the synthetic ketones, of known *trans* configuration, are nearly the same before and after prolonged irradiation indicates that the photochemical equilibrium mixture contains mainly *trans* isomer. Attempts to add aldehydes to monosubstituted acetylenes (benzaldehyde to phenylacetylene, butyraldehyde to 1-hexyne and benzaldehyde to 1-hexyne) resulted in the formation of the symmetrical acylolins rather than the expected 1:1 adducts.

The peroxide induced addition of aliphatic aldehydes to acetylenes to give 1,4-diketones by combination of two molecules of aldehyde with one molecule of acetylene has recently been reported.⁴ To rationalize their results the authors have adopted a radical-chain mechanism initiated by RC=O which had been postulated previously⁵ for the photochemical addition of aliphatic aldehydes to terminal olefins. It is known⁵ that aromatic

aldehydes undergo such additions with considerable difficulty and it does not seem possible to construct a mechanism directly related to this one which would be capable of accommodating the changes outlined above. The most reasonable scheme to rationalize the formation of α,β -unsaturated ketones seems to be



(1) Conversion of the aromatic carbonyl compound to the biradical triplet state (I, II) by absorption of light, followed by (2) formation of the corresponding oxetenes (III, IV) and (3) decomposition of these intermediates to either products (V, VI) or starting materials. An attempt has been made to isolate III but no evidence for its presence in the products of the reaction could be obtained.

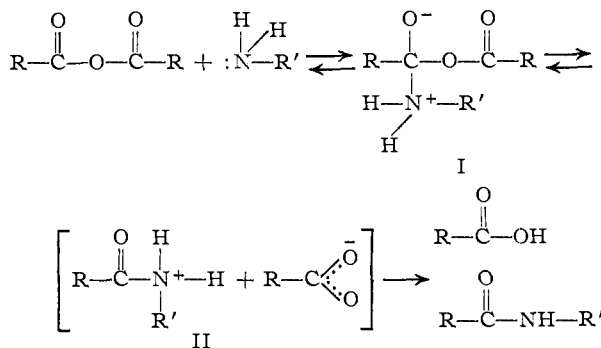
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
 MASSACHUSETTS INSTITUTE OF TECHNOLOGY G. BÜCHI
 CAMBRIDGE, MASSACHUSETTS JAMES T. KOFRON
 E. KOLLER
 DAVID ROSENTHAL

RECEIVED JANUARY 11, 1956

CONCERNING THE MECHANISM OF THE REACTION OF ANHYDRIDES WITH AMINES

Sir:

Data from several sources^{1,2,3} can be used to formulate the following general scheme for reactions of anhydrides with amines and other nucleophiles.



We wish to report data which throw considerable

- (1) E. Berliner and L. Altschul, *This Journal*, **74**, 4110 (1952).
- (2) V. Gold, J. Hilton and E. Jefferson, *J. Chem. Soc.*, 2756 (1954).
- (3) C. Bunton, T. Lewis and D. Llewellyn, *Chem. and Ind.*, 1154 (1954).

(4) H. H. Schlubach, V. Franzen and E. Dahl, *Ann.*, **587**, 124 (1954).

(5) M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

light on the effect of solvent on this reaction scheme (Table I).

TABLE I^a

Compound	Solvent	Atom % excess O ¹⁸			
		Found	Calculated No equil.	Equil.	
Benzoic Anhydride		1.32	1.30		
Benzanilide	ether	0.44	0.43	0.66	0.44
Benzoic Acid	ether	.87	.88	.66	.88
Benzanilide	water/acetone	.61	.60	.66	.44
	2 1				
Benzoic Acid	water/acetone	.70	.70	.66	.88
	2 1				
Benzamide	ammonia	.66	.65	.66	.44
Benzoic Acid	ammonia	.66	.65	.66	.88

^a Analyzed by the method of W. Doering and E. Dorfman, *THIS JOURNAL*, **75**, 5595 (1953).

When benzoic anhydride labeled in one carbonyl with oxygen-18 is treated with liquid ammonia, benzamide and benzoic acid each containing 50% of the original label are obtained. These results show that the carbonyl oxygen of the amide was a carbonyl oxygen in the anhydride; therefore decomposition of II to products is much faster than return to starting materials. Such a result is not unexpected as ammonia, the solvent, can react with the cation of II to give products. The same anhydride reacts with aniline in ether to give benzanilide containing 33% of the label and benzoic acid containing 67%, a result which can only arise if all of the oxygens in the anhydride become equivalent during the reaction. In this case reversion to starting materials from II could lead to equilibration of the oxygens. Such a process seems reasonable as the most effective base for completing the reaction is benzoate ion. The mode of decomposition of II will be controlled by the nucleophilicity of the benzoate ion as compared to its base strength. In this case, then, return, *i.e.*, nucleophilic displacement, is faster than proton transfer. Such an observation is in accord with the known properties of carboxylate ions, their nucleophilic properties being disproportionately greater than their base strength.⁴ Equilibration of the anhydride oxygens could have taken place by reaction with ether to form the oxonium salt. A control experiment in which the anhydride was first treated with ether, reisolated, and then converted to benzanilide in water/acetone (2:1) showed that no equilibration occurred in ether. When the original anhydride was treated with aniline in water/acetone, a small amount of equilibration took place. Return from II, or attack by benzoic acid formed during the reaction on unreacted benzoic anhydride could equally well account for this equilibration. The equilibration found in the ether experiments could possibly have arisen by attack of initially formed benzoic acid on unreacted benzoic anhydride. This reaction would have to be much faster than the conversion to benzanilide. When molar quantities of benzoic anhydride, aniline, radioactive benzoic acid and

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, pp. 451.

dimethylaniline (added to promote ionization of the acid) were allowed to react in ether, the benzanilide obtained contained 15% of the radioactivity calculated for complete exchange of all benzoyl containing species.⁵ Since the concentration of benzoic acid was much greater in this experiment than in the oxygen-18 equilibration studies, only a very small amount of the oxygen equilibration can arise through an intermolecular reaction involving benzoic acid. The carbon-14 exchange found could have either occurred by attack on benzoic anhydride, II or both. A control experiment without aniline showed that benzoic anhydride undergoes a slow exchange with radioactive benzoic acid under these conditions. Further work on these reactions is now in progress; particular attention is being devoted to the nature and properties of II in various solvents.

(5) We wish to thank Dr. A. P. Wolf of the Brookhaven National Laboratory for his aid in carrying out these experiments.

SCHOOL OF CHEMISTRY
RUTGERS UNIVERSITY
NEW BRUNSWICK, N. J.

DONALD B. DENNEY

STERLING CHEMISTRY LABORATORY
YALE UNIVERSITY
NEW HAVEN, CONN.

MICHAEL A. GREENBAUM

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STRUCTURE OF DITHIONITE

Sir:

The structure of the dithionite anion has been established by X-ray analysis of crystals of anhydrous sodium dithionite (hydrosulfide, hydrosulfite), Na₂S₂O₄. The crystals are monoclinic, $a = 6.404 \pm 0.0045 \text{ \AA.}$, $b = 6.559 \pm 0.0028 \text{ \AA.}$, $c = 6.586 \pm 0.0045 \text{ \AA.}$, $\beta = 119^\circ 31' \pm 0^\circ 02'$, space group P2/c, with four formula units of NaSO₂ in the unit cell. The space-group conditions require the doubled unit, Na₂S₂O₄, to possess either a center of symmetry or a two-fold rotation axis parallel to b .

The details of the structure have been determined and refined by repeated $F_0 - F_c$ Fourier projections¹ down the three axes which led eventually to disagreement factors $R = \Sigma |F_0 - F_c| / \Sigma |F_0|$ of 0.098, 0.063 and 0.106 for $(hk0)$, $(h0l)$, and $(0kl)$ reflections, respectively. The final atomic positions have estimated standard deviations of 0.008 Å. for sulfur, 0.011 Å. for sodium and 0.015 Å. for oxygen. The anion has approximate C_{2v} symmetry, the two independent S-O distances (1.496 Å. and 1.515 Å.) and O-S-S angles (98°01' and 99°23') not differing significantly. The S-S distance, 2.389 Å., is much longer than that in a typical disulfide bond, 2.08 Å.² Pauling's relationship between covalent radius and bond number, $-\Delta R(n) = 0.353 \log n^3$, leads to a bond number n of 0.36.

The dithionite anion can thus be regarded as a pair of SO₂⁻ units linked by a weak S-S bond. Although the existence of the free radical anion SO₂⁻ has not been demonstrated directly, the rapid exchange of S³⁵ between dithionite and sulfur

(1) W. Cochran, *Acta Cryst.*, **4**, 81, 408 (1951).

(2) S. C. Abrahams, *ibid.*, **7**, 428 (1954).

(3) L. Pauling, *THIS JOURNAL*, **69**, 542 (1947).