carried out polymerizations with a highly purified anhydride[5] (C in Fig. 2) to which 0.67 and 5.0 mole % of *n*-hexylamine hydrochloride had been added (D and E in Fig. 2). The results show that this adduct eliminates the second propagation step and produces pseudo first-order reactions which bracket the one reported by Ballard and Bamford[1] as "the most reliable thus far obtained." It is evident, therefore, that the results of Ballard and Bamford can be reproduced by impure anhydride or by the addition to highly purified anhydride of one of the impurities removed during its purification. Thus, the sensitivity of this effect to contamination of the anhydride suggests that the presence of *some* impurity is the most likely explanation of their results. Space prevents taking up other possibilities that could arise from not carrying out the purification of the anhydride at −30° as described.[5] Moreover, the premise of Ballard and Bamford concerning the uniqueness of the sublimation in anhydride purification appears invalid inasmuch as we have observed the two successive propagation steps to be even more dramatically exhibited in L-leucine N-carboxy anhydride, both before and after sublimation of the product purified as described.[5] Consequently, we cannot concede that Ballard and Bamford's failure to observe the reported kinetic effect is evidence against its existence.

(2) The kinetic effect we have reported must, of course, be reflected in the molecular weight distribution of the product. In this case, the distribution must be exceedingly broad as we have reported.[2] In case C, for example, the number average DP is 20 and the weight average DP is 170.[6] If, on the other hand, the second propagation step is suppressed as in Case D, the distribution should narrow. This is indeed observed: for case D, $DP_w = 46$, $DP_N = 17.5$. The analysis of the products, therefore, is seen to support the original contention that two successive rate constants are observed under the conditions reported.

We wish to thank Dr. E. R. Blout for his very helpful collaboration in this work.

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(6) These measurements were made by Mr. J. C. Mitchell in this Laboratory using the Archibald approach-to-equilibrium technique in ultracentrifugation.

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RECEIVED FEBRUARY 1, 1957

AN ALLEGED FREE RADICAL REACTION IN WHICH BENZENE UNDERGOES ATTACK MORE READILY THAN NITROBENZENE

Sir:

Wieland and Meyer[1] reported that the reaction of triphenylmethyl radical with aromatic substrates, in the presence of benzoyl peroxide, afforded *para*-substituted tetraphenylmethanes. The discovery[2] that these substances were, in reality, *meta* isomers, prompted us to reinvestigate the reaction.

Although nitrobenzene as a substrate was not studied in the original Wieland[1] work, it seemed of special interest to us because of its propensity to participate in free radical reactions with greater ease than benzene itself $(C_6H_5NO_2/C_6H_6)K = 4$).[3]

We found that when triphenylmethyl radicals (in the presence of benzoyl peroxide) were permitted to compete for benzene and nitrobenzene (equimolar mixture) the only products that could be detected were tetraphenylmethane (10%) and *p*-bistriphenylmethylbenzene, m.p. 330° (9%). (The latter was identical in m.p. and infrared spectrum with material prepared by an independent synthesis.) Both infrared analysis of the crude reaction product and C^{14}-tracer experiments confirmed that nitrotetraphenylmethanes were formed only in trace amounts, if indeed at all.

In conjunction with this work, it was also found that triphenylmethyl radical is not consumed to any appreciable extent by reaction with the nitro function of nitrobenzene in the *absence* of benzoyl peroxide. This is in contradiction to the report by Hammond and Ravve[4] that a quantitative reaction occurs, to afford triphenylcarbinol, azobenzene and phenol among other products.

After a benzene solution of triphenylmethyl (prepared in benzene from triphenylmethyl chloride and mercury) and nitrobenzene had been exposed to diffuse daylight for 24 hours, practically all of the triphenylmethyl was still present and infrared analysis showed the complete absence of azobenzene. Trace amounts of phenol could be detected after a reaction period of 4 days, but its formation was independent of the presence of nitrobenzene since it was also found in mixtures containing only triphenylmethyl and benzene.

The formation of phenol might reasonably be explained by assuming that phenyl radicals are produced in some manner, as postulated by Hammond and Ravve, but the implication[4] that these radicals then abstract oxygen from nitrobenzene appears to be invalid. The presence of trace amounts of atmospheric oxygen seems to afford a better explanation for the phenol production.

We are currently investigating the cause of the surprising reversal of relative reactivity of trityl radicals toward benzene and nitrobenzene. Several possibilities occur to us at this time. (1) Perhaps the Wieland reaction, which has been traditionally considered free radical in nature is instead ionic. (2) The trityl radical may have some carbonium ion character due to the I effects of the three phenyl groups.[5] (3) An ion-pair type complex might form rapidly and reversibly between the easily oxidized trityl radical and nitrobenzene, thus vitiating normal trityl radical attack on that nucleus.

While the first of these explanations cannot be dismissed at this time, it does not seem like an attractive possibility. The Baeyer–Villiger reaction,[6] which almost certainly proceeds *via* a tritylcarbonium ion, occurs only with activated nuclei. Even toluene does not react in a four day period.[2] The

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(1) H. Wieland and A. Meyer, *Ann.*, **551**, 249 (1942).

(2) R. A. Benkeser and R. Gosnell, THIS JOURNAL, **78**, 4914 (1956).

(3) D. H. Hey, *et al.*, *J. Chem. Soc.*, 2094 (1952).

(4) G. S. Hammond and A. Ravve, THIS JOURNAL, **73**, 1891 (1951).

(5) See R. L. Dannley and M. Sternfeld, *ibid.*, **76**, 4543 (1954), where this general concept was proposed.

(6) A. Baeyer and V. Villiger, *Ber.*, **35**, 3018 (1902).

Wieland reaction, on the other hand, proceeds successfully with toluene, benzene, chlorobenzene and ethylbenzoate.

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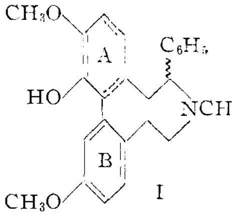
RECEIVED MARCH 18, 1957

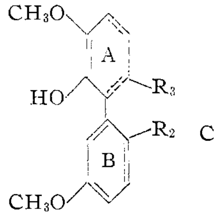
ASYMMETRIC INDUCTION AND ABSOLUTE CONFIGURATION IN THE BIPHENYL SERIES

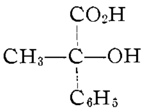
Sir:

Methylmagnesium iodide converts the phenylglyoxylates of phenyldihydrothebaine (I) and its derivatives (IIa-c) (absolute configurations[1] as shown) to atrolactic esters. Saponification and isolation without optical fractionation give (−)-atrolactic acid (III) (absolute configuration[2] as shown) in optical yields of 70% from I and 91, 89, and 93%, respectively, from IIa-c. These are the highest optical yields known in the reactions of α-ketoesters with Grignard reagents.



I



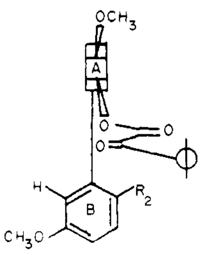


$$\begin{array}{c} CO_2H \\ | \\ CH_3—C—OH \\ | \\ C_6H_5 \end{array}$$

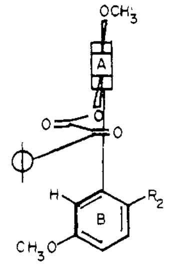
III

IIa, $R_2 = CH{=}CH_2$; $R_3 = CH_2CH(C_6H_5)N(CH_3)_2$
b, $R_2 = C_2H_5$; $R_3 = CH_2CH(C_6H_5)N(CH_3)_2$
c, $R_2 = CH{=}CH_2$; $R_3 = CH{=}CHC_6H_5$

The formation of III is most reasonably explained on the consideration that most of the product is derived from the two most stable ground state conformations IV and V, in which repulsive interactions are minimized by disposition of the two keto groups coplanar-transoid and the plane of the phenylglyoxylate chain as far away as possible from the ring A methoxyl and ring B, *i.e.*, perpendicular to ring A and at a dihedral angle of 60° with respect to ring B. Approach to the keto carbonyl group in IV and V by the attacking methyl must occur from the direction of ring A, since the underside of the keto group is shielded by ring B. If the rotational barrier between IV and V is high, the major proportion of the product is derived from V, which is more stable than IV because the phenylglyoxylate chain interferes with H instead of R. If the rotational barrier is low compared to the energy of activation for chemical reaction, the product proportions are controlled by the difference in free energy between the transition states derived from IV and V.[3] That from V is the more stable, since in it, the compression of the groups attached to the keto carbonyl as the latter begins to become tetrahedral is against H, whereas in that from IV, this compression is against the large group R. When the effective bulk of R increases (I → II), the stereoselectivity increases. A number of alternative interpretations ascribing special stability to other conformations because of chelate complexing, appear less probable. In particular, the conformation in which each carbonyl group is complexed with a ring methoxyl, and the plane of the phenylglyoxylate residue is perpendicular to ring A and parallel to ring B, would also lead to III. However, in order to explain on this basis the fact that the stereoselectivities with the phenylglyoxylates of IIa-c are 3.5 to 5.8 times greater than with that of I it is necessary to assume that the degree of complexing is less in the latter case. There is no obvious reason why this should be so and, at present, this alternative, while not rigorously excluded, appears unlikely.

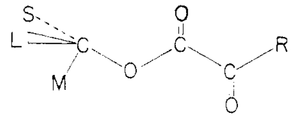


IV



V

In elegant studies, McKenzie, Prelog, Turner and their respective co-workers have examined a large number of reactions of the general type $R_1COCO_2R_a + R_2MgX \rightarrow \rightarrow R_1R_2C(OH)CO_2H$. In eighteen such cases, complete resolution data are available on the product hydroxyacid and, using these, we have now calculated optical yields.[4] For a fixed asymmetric group (R_a), the optical yield is quite insensitive to the size of the incoming group (R_2), but becomes larger as the size of the group (R_1) *already attached* to the keto group increases. This phenomenon requires modification of the previously proposed[5] shielding effect theory of asymmetric induction in α-ketoesters. It is most readily encompassed by the hypothesis that the relative contribution to the total product made by conformation VI diminishes with increasing size of R_1 because of compression effects of the type discussed above.



VI

We are indebted to the National Science Foundation for financial support.

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(1) J. A. Berson, THIS JOURNAL, **78**, 4170 (1956).

(2) *Cf.* J. H. Brewster, *ibid.*, **78**, 4061 (1956).

(3) *Cf.* D. Y. Curtin, *Rec. Chem. Progress*, **15**, 111 (1954); D. Y. Curtin and M. C. Crew, THIS JOURNAL, **77**, 354 (1954).

(4) Complete literature references will be given in a forthcoming publication.

(5) V. Prelog, *Bull. soc. chim.*, 987 (1956), and references cited therein.

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RECEIVED FEBRUARY 9, 1957

CYANOCARBON CHEMISTRY—SYNTHESIS AND CHEMISTRY OF TETRACYANOETHYLENE

Sir:

Investigation of cyanocarbons, compounds containing only —C≡N groups attached to carbon,